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Państwowe Wydawnictwo Naukowe

A generalization of the theory of distributions

by

W. SŁOWIKOWSKI

Presented by K. KURATOWSKI on October 19, 1954

1. There are several different approaches to the problem of generalizing the notion of function and its derivative. The purpose of this paper is to give a general theory of algebraic extension of certain algebraic systems so that we obtain as particular cases of this theory: Schwartz's theory of distributions [2], the theory of Mikusiński [1] and the classical method of extension of an integral domain to a field of rationals *). This theory is a generalization of Sikorski's [3] approach to Schwartz's theory. It may be applied to the semigroup of linear operators in locally-convex space.

2. An *operator system* is an ordered pair $\mathfrak{A} = (S, X)$, where:

a) S is a commutative semigroup written multiplicatively with the unit element I (the cancelation law is assumed),

b) X is a commutative group written additively,

c) with each element $A \in S$ there is associated a subgroup $G(A)$ of X and with each pair $A \in S$ and $x \in G(A)$ there is associated an element $y = Ax \in X$ (the composition of A and x) in such a way, that:

1) the mapping $y = Ax$ is a homomorphism of $G(A)$ onto the whole group X ,

2) if $x \in G(AB)$, where $A, B \in S$, then $x \in G(B)$, $Bx \in G(A)$ and $(AB)x = A(Bx)$.

If $G(A) = X$ for each $A \in S$, then A is said to be *algebraically closed*.

$\mathfrak{A}$ is said to be a *linear operator system* if X is a linear space and the condition $x \in G(A)$ implies $\lambda x \in G(A)$ and $A(\lambda x) = \lambda(Ax)$.

3. An *ideal* of an operator system (a linear operator system) $\mathfrak{A} = (S, X)$ is a mapping $\mathfrak{I}$ defined on S such that its values $\mathfrak{I}(A)$ are subgroups

*) J. G. Mikusiński was also aware of another common generalization of his own and Schwartz's theories.

(linear subspaces) of X and, for every $A, B \in S$ and $x \in G(A)$,

- 1) $Ax \in \mathfrak{I}(B)$ if and only if $x \in \mathfrak{I}(AB)$; and 2) $\mathfrak{I}(B) \subset \mathfrak{I}(AB)$.

For instance, if $\mathfrak{I}(A) = X$ for every $A \in S$, then $\mathfrak{I}$ is an ideal.

If $\mathfrak{I}_1$ and $\mathfrak{I}_2$ are ideals, we write $\mathfrak{I}_1 \subset \mathfrak{I}_2$ whenever $\mathfrak{I}_1(A) \subset \mathfrak{I}_2(A)$ for every $A \in S$.

If $\{\mathfrak{I}_i\}$ is a set of ideals, then the function $\mathfrak{I}$, where $\mathfrak{I}(A) = \bigcap_i \mathfrak{I}_i(A)$, is also an ideal. Therefore every operator system has a *minimal ideal*.

An ideal $\mathfrak{I}$ is called a *zero ideal* if $\mathfrak{I}(I) = \{0\}$.

4. Let $\mathfrak{A} = (S, X)$ and $\mathfrak{A}' = (S', X')$ be two operator systems. A pair $\mathfrak{H} = (H, h)$ is said to be a *homomorphism (isomorphism)* of $\mathfrak{A}$ into $\mathfrak{A}'$ if H is a homomorphism (isomorphism) of S into S' , h is a homomorphism (isomorphism) of X into X' , and $h(Ax) = H(A)h(x)$ for $A \in S$, $x \in G(A)$. If $\mathfrak{H} = (H, h)$ is a homomorphism of $\mathfrak{A}$ into $\mathfrak{A}'$ and $\mathfrak{I}'$ is an ideal of $\mathfrak{A}'$, then the formula

$$\mathfrak{I}(A) = \bigcup_{x \in X} \{h(x) \in \mathfrak{I}'[H(A)]\} \quad \text{for } A \in S$$

defines an ideal of $\mathfrak{A}$ denoted by $\mathfrak{H}^{-1}\mathfrak{I}'$. If, for an ideal $\mathfrak{I}'$ of $\mathfrak{A}'$, $\mathfrak{H}^{-1}\mathfrak{I}'$ is a zero ideal and H is an isomorphism, then $\mathfrak{H}$ is an isomorphism.

5. THE FUNDAMENTAL ALGEBRAIC THEOREM. *For every operator system $\mathfrak{A} = (S, X)$ and every ideal $\mathfrak{I}$ of $\mathfrak{A}$ there is an algebraically closed operator system $\mathfrak{A}' = (S', X')$ and a homomorphism $\mathfrak{H} = (H, h)$ of $\mathfrak{A}$ into $\mathfrak{A}'$, such that*

- (i) $\mathfrak{I} = \mathfrak{H}^{-1}\mathfrak{I}'$, where $\mathfrak{I}'$ is the minimal ideal of $\mathfrak{A}'$,
- (ii) H is an isomorphism of S onto S' (therefore we shall often write $S' = S$),
- (iii) for each $y \in X'$ there is $A \in S$ and $x \in X$, such that $y = H(A)h(x)$.

The operator system $\mathfrak{A}'$ is uniquely determined (up to isomorphism) by $\mathfrak{A}$ and $\mathfrak{I}$ and is denoted by $\mathfrak{A}/\mathfrak{I}$ (quotient operator system). The corresponding homomorphism is called the *natural homomorphism*. If $\mathfrak{I}$ is a zero ideal, then the natural homomorphism $\mathfrak{H}$ is an isomorphism, i. e. $\mathfrak{A}/\mathfrak{I}$ is an extension of $\mathfrak{A}$. If $\mathfrak{A}$ is linear, so is $\mathfrak{A}/\mathfrak{I}$.

6. Examples. A) Let X be the additive group of all integers and S the multiplicative semigroup of all numbers $1/m$, $m=1, 2, \dots$. The composition is the usual multiplication. The mapping $\mathfrak{I}(A) = \{0\}$ is the zero ideal (also the minimal ideal) and $\mathfrak{A}/\mathfrak{I} = (S, X')$, where X' is the field of all rational numbers.

B) Let X be the additive group of all continuous functions $x(t)$ defined for $t \geq 0$ and S — the set of these functions except the zero function.

The product of two elements $A, B \in S$ is the convolution:

$$\int_0^t A(t-\tau) B(\tau) d\tau.$$

The composition $y = Ax$ ($A \in S, x \in X$) is a function $y(t)$ such that $x(t)$ is the convolution of $A(t)$ and $y(t)$, i. e.

$$x(t) = \int_0^t A(t-\tau)y(\tau)d\tau.$$

The mapping $\mathfrak{I}(A) = \{0\}$ is the zero ideal (also the minimal ideal) and $\mathfrak{U}/\mathfrak{I} = (S, X')$, where X' is the field of Mikusiński's operators.

C) Examples A) and B) may be generalized as follows: Let X be a commutative ring (with the unit element) and let S be the semigroup of all elements $A \in S$ which are not divisors of zero. An element y is the composition of $A \in S$ and $x \in X$, whenever x is the usual product of A and y . The mapping $\mathfrak{I}(A) = \{0\}$ is the zero ideal (also the minimal ideal) and $\mathfrak{U}/\mathfrak{I} = (S, X')$, where X' is the ring of all quotients x/A , where $x \in X$ and $A \in S$. If X has no divisors of zero, then X' is the least field containing the ring X .

D) Let X be the linear space of all continuous functions $x(t)$ defined for real t , and let S be the set of differential operators

$$\frac{d^n}{dt^n}, \quad n = 0, 1, \dots$$

$G(d^n/dt^n)$ is the set of all functions which have continuous n -th derivatives. The mapping

$$\mathfrak{I}\left(\frac{d^n}{dt^n}\right) = \text{the set of all polynomials of degree } < n$$

is the zero ideal and $\mathfrak{U}/\mathfrak{I} = (S, X')$, where X' is the set of all Schwartz distributions of finite order.

The more-dimensional distributions of finite order can be obtained in a similar way (only the definition of $\mathfrak{I}\left(\frac{\partial^n}{\partial t_1 \dots \partial t_n}\right)$ is more complicated).

7. A linear operator system $\mathfrak{U} = (S, X)$ is said to be *locally convex* if X is a locally convex space and all the homomorphisms $A \in S$ (of $G(A)$ onto X) are continuous.

THE FUNDAMENTAL TOPOLOGICAL THEOREM. Let $\mathfrak{U} = (S, X)$ be a linear operator system such that X is a locally convex linear space. Then there is an ideal $\mathfrak{I}_0$ of A such that:

- 1° $\mathfrak{U}/\mathfrak{I}_0 = (S_0, X_0)$ is a locally convex operator system;
- 2° the natural homomorphism of X into X_0 is continuous;
- 3° if $\mathfrak{I}_1$ is an ideal and $\mathfrak{U}/\mathfrak{I}_1 = (S_1, X_1)$ is a locally convex operator system and the natural homomorphism of X into X_1 is continuous, then $\mathfrak{I}_0 \subset \mathfrak{I}_1$ and there is a homomorphism of $\mathfrak{U}/\mathfrak{I}_0$ onto $\mathfrak{U}/\mathfrak{I}_1$ such that the corresponding mapping of X_0 into X_1 is continuous.

A similar theorem is also valid if the neighbourhood topology is replaced by a sequential one.

8. Example. Let X be a locally convex linear space and S be a certain commutative semigroup of linear operators (which are, in general, non-continuous) each of which maps a linear subspace of X onto X . Further let F be the family of all functionals f defined on $S \times X$ such that

- 1) if $A \in S$ is fixed, then $f(A, x)$ is a continuous linear functional on X ;
- 2) $f(A, Bx) = f(AB, x)$ for every $A, B \in S$ and $x \in G(B)$.

Then the ideal $\mathfrak{I}$, where

$$\mathfrak{I}(A) = E \left(\prod_{x \in X} \prod_{f \in F} f(A, x) = 0 \right),$$

is the same as the ideal defined in the fundamental topological theorem. In the case where: X is the space of all continuous functions defined on the n -dimensional Euclidean space, S is the semigroup of operators

$$A = \frac{\partial^m}{\partial t_1^{m_1} \partial t_2^{m_2} \dots \partial t_n^{m_n}},$$

and

$$f(A, x) = (-1)^m \int A \varphi(t) x(t) dt,$$

where φ is an infinitely differentiable function with compact carrier, then $\mathfrak{U}/\mathfrak{I} = (S, X')$ where X' is the space of all Schwartz distributions of finite order.

9. For algebraic fullness of the theory of operator systems the following theorem is needed:

Let $\mathfrak{A}_1$ and $\mathfrak{A}_2$ be two operator systems (linear operator systems), let $\mathfrak{I}_1$ and $\mathfrak{I}_2$ be two ideals of $\mathfrak{A}_1$ and $\mathfrak{A}_2$, let $\mathfrak{A}_1/\mathfrak{I}_1$ and $\mathfrak{A}_2/\mathfrak{I}_2$ be the quotient operator systems (the linear operator-systems) and let $\mathfrak{H}_1, \mathfrak{H}_2$ be corresponding natural homomorphisms. If $\mathfrak{H} = (H, h)$ is a homomorphism of $\mathfrak{A}_1$ into $\mathfrak{A}_2$, then $\mathfrak{I}_1 \subset \mathfrak{H}^{-1}\mathfrak{I}_2$ if and only if there is a homomorphism $\mathfrak{H}^*$ of $\mathfrak{A}_1/\mathfrak{I}_1$ into $\mathfrak{A}_2/\mathfrak{I}_2$ such that $\mathfrak{H}^*\mathfrak{H}_1 = \mathfrak{H}_2\mathfrak{H}$. The homomorphism $\mathfrak{H}^*$ is uniquely determined by $\mathfrak{H}, \mathfrak{H}_1, \mathfrak{H}_2$ and is an isomorphism if and only if $\mathfrak{H}$ is an isomorphism and $\mathfrak{H}^{-1}\mathfrak{I}_2 \subset \mathfrak{I}_1$.

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On σ -complete Boolean algebras

by

R. SIKORSKI

Presented by K. KURATOWSKI on November 26, 1954

E. Marczewski has posed the question, whether it is possible to distinguish (in the class of all σ -complete Boolean algebras $\mathbf{B}$) the subclass of all σ -complete Boolean algebras isomorphic to σ -fields of sets, by means of a set of conditions $\{W_i\}$, each of which expresses a property of subsets $Z \subset \mathbf{B}$ of power $\bar{Z} \leq m$, where m is a fixed cardinal number. The purpose of this paper is to prove that the answer to this question is negative under some very general hypotheses about the form of the conditions $\{W_i\}$.

In the sequel, let m denote an arbitrary fixed infinite cardinal less than the first aleph inaccessible in the strict sense *).

If Z is a subset of a Boolean algebra $\mathbf{B}$, then $\mathbf{B}(Z)$ denotes the least subalgebra of $\mathbf{B}$ such that $Z \subset \mathbf{B}(Z)$ and if $a_t \in \mathbf{B}(Z)$ for each $t \in T$ (where the cardinal T is arbitrary) and a is the sum (product) of all the elements a_t in the algebra $\mathbf{B}$, then also $a \in \mathbf{B}(Z)$.

Suppose that each condition W_i (formulated, obviously, in terms of the theory of Boolean algebras) has the form of a formula **)

$$W_i = \prod_{F_1} \prod_{F_2} \dots \prod_{F_{k_i}} V_i,$$

where

$$F_1 = \{a_{1,t}\}_{t \in T_1}, \quad F_2 = \{a_{2,t}\}_{t \in T_2}, \quad \dots, \quad F_{k_i} = \{a_{k_i,t}\}_{t \in T_{k_i}}$$

are arbitrary indexed sets of elements of a considered Boolean algebra $\mathbf{B}$ and

$$(*) \quad \bar{T}_1 < m, \quad \bar{T}_2 < m, \quad \dots, \quad \bar{T}_{k_i} < m.$$

*) A cardinal $n > \aleph_0$ is called *inaccessible in the strict sense* if the conditions $n_t < n$, for every $t \in T$, and $\bar{T} < n$ imply that $\prod_{t \in T} n_t < n$.

**) $\prod$ denotes here the general quantifier. More exactly, the symbol $\prod_F$ should here be read: for every indexed set $F = \{a_t\}_{t \in T}$ of elements of $\mathbf{B}$, where $\bar{T} \leq m, \dots$

We suppose also that the condition V_i is satisfied by some indexed sets $F_1, F_2, \dots, F_{k_i}$ in a Boolean algebra $\mathbf{B}$ if and only if V_i is satisfied by the same indexed sets in the Boolean algebra $\mathbf{B}(Z)$ where $Z = F_1 + F_2 + \dots + F_{k_i}$. We assume here that the infinite Boolean operations in $\mathbf{B}(Z)$ are those in $\mathbf{B}$ restricted to $\mathbf{B}(Z)$, i. e. we call an element $a \in \mathbf{B}(Z)$ the sum (product) of an indexed set $a_i \in \mathbf{B}(Z)$, if and only if a is the sum (product) of elements a_i in the algebra $\mathbf{B}$.

Of course, we suppose also that each of the conditions W_i is satisfied in every Boolean algebra isomorphic to a σ -field of sets.

Under these hypotheses about the conditions $\{W_i\}$ the following theorem is true.

(i) *For each set of conditions $\{W_i\}$ there exists a σ -complete Boolean algebra $\mathbf{B}$ such that:*

- (a) *each of the conditions W_i is satisfied in $\mathbf{B}$;*
- (b) *$\mathbf{B}$ is not isomorphic to a σ -field of sets.*

To prove theorem (i) we shall first show that

- (ii) *There exists a σ -complete Boolean algebra $\mathbf{B}$, such that*
- (c) *if $Z \subset \mathbf{B}$ and $\bar{Z} \leq m$, then $\mathbf{B}(Z)$ is isomorphic to a totally additive field of sets,*
- (d) *$\mathbf{B}$ is not isomorphic to a σ -field of sets.*

The construction of the algebra $\mathbf{B}$ satisfying (ii) is a simple modification of an example *) given in my paper [2] § 3. It is sufficient to set $\mathbf{B} = \mathbf{S}/\mathbf{I}$, where $\mathbf{S}$ is the field of all subsets of a set X , $\bar{X} > 2^m$, and $\mathbf{I}$ is the ideal of all sets $Y \subset X$ such that $\bar{Y} \leq 2^m$.

In fact, by a general theorem (see [2], p. 253, th. 2.3), $\mathbf{B} = \mathbf{S}/\mathbf{I}$ is not isomorphic to a σ -field of sets. Let $[A]$ be the element of $\mathbf{S}/\mathbf{I}$ determined by a set $A \subset X$ (i. e. $[A]$ is the coset of $\mathbf{S}/\mathbf{I}$ such that $A \in [A]$). Let $Z \subset \mathbf{S}/\mathbf{I}$, $\bar{Z} \leq m$. For every $a \in Z$ let A_a be a subset of X such that $a = [A_a]$. Let $\mathbf{S}_0$ be the least 2^m -additive field (of subsets of X) containing all the sets A_a . The algebra $\mathbf{B}_0 = \mathbf{S}_0/\mathbf{I}$ is 2^m -complete. Since $\bar{\mathbf{B}}_0 \leq 2^m$, $\mathbf{B}_0$ is complete. Consequently $\mathbf{B}_0 = \mathbf{B}(Z)$. The algebra $\mathbf{B}_0$ is atomic, viz. the atoms of $\mathbf{B}_0$ are the elements $[A]$, where A is an atom of the field $\mathbf{S}_0$ and $\bar{A} > 2^m$. Thus $\mathbf{B}_0 = \mathbf{B}(Z)$ is isomorphic to a completely additive field of sets (see [3], p. 198).

The algebra $\mathbf{B} = \mathbf{S}/\mathbf{I}$ also satisfies theorem (i). In fact, let V_i , $F_1, F_2, \dots, F_{k_i}$ have the meaning defined above (in particular, we assume the inequalities (*)). The property V_i is satisfied by arbitrary indexed sets $F_1, F_2, \dots, F_{k_i}$ in $\mathbf{B}(Z)$, where $Z = F_1 + F_2 + \dots + F_{k_i}$, since $\mathbf{B}(Z)$ is

*) This example was also used by Enomoto ([1], p. 108) to prove a theorem weaker than theorem (i).

isomorphic to a σ -field of sets. Consequently, $F_1, F_2, \dots, F_{k_i}$ satisfies also V_i in $\mathbf{B}=\mathbf{S}/\mathbf{I}$, i. e. W_i is true in $\mathbf{B}$.

It is obvious that the above consideration remains true if we replace the σ -completeness by $\aleph$ -completeness where $\aleph$ is an infinite cardinal.

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A remark on the Mazur-Orlicz theory of summability

by

R. SIKORSKI

Presented by S. MAZUR on November 26, 1954

The purpose of this paper*) is to show that the Mazur-Orlicz ([2], [3]) theory of summability (see also [7]) of sequences by Toeplitz methods is a particular case of a general algorithm which can be applied not only to sequences of numbers, but also to functions and (after some further modifications) to sequences of functions, etc. This algorithm also contains, as a particular case, the theory of continuous methods of summability, developed recently by Włodarski [5], [6]. More exactly, in this paper I shall generalize some theorems on consistency of methods. This generalization exhibits the known results in a clearer form (which is free of non-essential complicated formulas) and suggests some new applications (the general theory of summability of functions).

Let X be a fixed (B_0) -space (i. e. a linear complete metric space with a topology determined by a sequence of semi-norms — see Mazur and Orlicz [4]). Let Q_0 be a compact set of (finite or infinite) real numbers, such that the number $q_0 = \sup_{q \in Q_0} q$ is a cluster point (i. e. a non-isolated point) of Q_0 , and let $Q = Q_0 - (q_0)$. Let P_0 be a compact metric space, let p_0 be a cluster point of P_0 , let $P = P_0 - (p_0)$ and

$$P_n = \bigcup_{p \in P} (e(p, p_0) \geq 1/n) \quad \text{for } n = 1, 2, \dots$$

We suppose that with each number $q \in Q$ there is associated a continuous linear transformation T_q of X into X in such a way that (writing x_q instead of $T_q(x)$)

$$(a) \quad \lim_{q \rightarrow q_0} x_q = x \text{ in } X;$$

$$(b) \quad (x_q)_{q'} = x_{\min(q, q')} \text{ (i. e. } T_q T_{q'} = T_{q'} T_q = T_{\min(q, q')}).$$

We suppose also that with each point $p \in P$ there is associated a linear (but not necessarily continuous) functional f_p defined on the

*) Presented at the Group of Functional Analysis of the Mathematical Institute of the Polish Academy of Sciences in March 1954.

linear set X' of all the elements x_q (where $x \in X$ and $q \in Q$), in such a way that

(c) for each fixed $x \in X$, the function $f_{p,q}(x) = f_p(x_q)$ of variables p, q is continuous on $P \times Q$;

(d) for fixed $p \in P$ and $q \in Q$, the linear functional $f_{p,q}$ (defined on X) is continuous.

Each system $M = \langle X, Q, q_0, P, p_0, \{T_q\}_{q \in Q}, \{f_p\}_{p \in P} \rangle$, satisfying all the conditions mentioned above is called a *method of summability*. We shall assume that all these conditions are fulfilled.

The set X^0 of all elements $x \in X$ such that $f_p(x_q)$ converges almost uniformly on P (i. e. uniformly on each compact subset of P) for $q \rightarrow q_0$, is a (B_0) -space with the topology determined by all the semi-norms of X and by the following semi-norms:

$$\|x\|_k = \sup_{\substack{q \in Q \\ p \in P_k}} |f_p(x_q)| \quad (k=1, 2, \dots).$$

The completeness of X^0 follows from the fact that the set X_1 of all $x \in X$ such that $\|x\|_k < \infty$ for $k=1, 2, \dots$ is a (B_0) -space with the topology determined by the semi-norms of X and by the semi-norms $\|x\|_k$, and that X^0 is a closed subspace of X_1 (see also Zeller [7], p. 473).

By (b), X' is contained in X^0 . Setting $f_p(x) = \lim_{q \rightarrow q_0} f_p(x_q)$ we extend the definition of f_p onto X^0 . It follows from (c) and (d) that:

(i) For every fixed $p \in P$, $f_p(x)$ is a continuous linear functional on X^0 .

(ii) For every fixed $x \in X^0$, the function $f_p(x)$ of the variable p is continuous on P .

It follows from (a) that

(iii) If $q \rightarrow q_0$, then $x_q \rightarrow x$ in X^0 for every $x \in X$.

In fact, the number $|f_p(x_{q'}) - f_p(x_{q,q'})|$ is equal to zero if $q' \leq q$ and it is equal to $|f_p(x_{q'}) - f_p(x_q)|$ if $q' \geq q$. Consequently,

$$\|x - x_q\|_k = \sup_{\substack{q' \in Q \\ p \in P_k}} |f_p(x_{q'}) - f_p(x_{q,q'})| \rightarrow 0$$

if $q \rightarrow q_0$ ($k=1, 2, \dots$).

The *field* of the method M is the linear space X^* of all $x \in X^0$ such that the limit $\lim_{p \rightarrow p_0} f_p(x)$ (denoted by $f(x)$ or $f_p(x)$) exists and is finite.

The field X^* is a (B_0) -space with the topology determined by all the semi-norms of X^0 and by the semi-norm $\|x\|^* = \sup_{p \in P} |f_p(x)|$. According to (i),

(iv) f is a continuous linear functional on X^* .

It follows immediately from the definition of the topology in X^* and from (ii) that

(v) Each linear continuous functional φ on X^* is of the form

$$(*) \quad \varphi(x) = F(x) + \int_{P_0} f_p(x) d\nu(p),$$

where F is a continuous linear functional on X^0 and ν is a finite signed measure (i. e. an enumerably additive set function) on the class of all Borel subsets of P_0 .

Let Z be the set of all $x \in X^*$ such that

$$(1) \quad f(x_q) = \lim_{p \rightarrow p_0} f_p(x_q) \text{ exists for each } q \in Q;$$

$$(2) \quad \lim_{q \rightarrow q_0} f(x_q) \text{ exists};$$

$$(3) \quad \sup_{\substack{q \in Q \\ p \in P}} |f_p(x_q)| < \infty.$$

(vi) If φ is a continuous linear functional on X^* of the form (*), and $x \in Z$, then

$$\varphi(x) = \lim_{q \rightarrow q_0} \varphi(x_q) + \nu(p_0) (f(x) - \lim_{q \rightarrow q_0} f(x_q)).$$

In fact, it follows from (1)–(3) that

$$\begin{aligned} \int_{P_0} f_p(x) d\nu(p) &= \int_P f_p(x) d\nu(p) + f(x) \nu(p_0) \\ &= \int_P \lim_{q \rightarrow q_0} f_p(x_q) d\nu(p) + f(x) \nu(p_0) = \lim_{q \rightarrow q_0} \int_P f_p(x_q) d\nu(p) + f(x) \nu(p_0) \\ &= \lim_{q \rightarrow q_0} \int_{P_0} f_p(x_q) d\nu(p) + \nu(p_0) (f(x) - \lim_{q \rightarrow q_0} f(x_q)), \end{aligned}$$

and $\lim_{q \rightarrow q_0} F(x_q) = F(x)$ (since $x_q \rightarrow x$ in X^0), which implies (vi).

Notice that (in contrast to (iii)) x_q does not converge, in general, to x in X^* . On the other hand, it follows from (vi) that

(vii) If $x \in Z$ and $f(x) = \lim_{q \rightarrow q_0} f(x_q)$, then $x_q \rightarrow x$ weakly in X^* for $q \rightarrow q_0$.

Setting $x - \lambda x^0$ instead of x in (vii), we obtain

(viii) If there is an element $x^0 \in Z$ such that $f(x^0) \neq \lim_{q \rightarrow q_0} f(x_q^0)$, then, for each $x \in Z$, $(x - \lambda x^0)_q + \lambda x^0 \rightarrow x$ weakly in X^* for $q \rightarrow q_0$, where λ is the number such that $f(x) - \lim_{q \rightarrow q_0} f(x_q) = \lambda (f(x^0) - \lim_{q \rightarrow q_0} f(x_q^0))$.

Let $\mathcal{M} = \langle \mathfrak{X}, \mathfrak{Q}, q_0, \mathfrak{P}, p_0, \{\mathfrak{X}_q\}_{q \in \mathfrak{Q}}, \{\mathfrak{f}_p\}_{p \in \mathfrak{P}} \rangle$ be another method of summability. Let $\mathfrak{X}^0, \mathfrak{X}^*, \mathfrak{Z}, \mathfrak{f}, \dots$ denote the analogues of $X^0, X^*, Z, f, \dots$ constructed for the method $\mathcal{M}$. The method $\mathcal{M}$ is said to be *stronger* than M if $X \subset \mathfrak{X}$ topologically (i. e. $X \subset \mathfrak{X}$ set-theoretically, and if $x_n \rightarrow x$ in X , then also $x_n \rightarrow x$ in $\mathfrak{X}$) and $X^* \subset \mathfrak{X}^*$ (set-theoretically).

(ix) If $\mathfrak{M}$ is stronger than M , then also $X^* \subset \mathfrak{X}^*$ topologically, i. e., the identical mapping of X^* into $\mathfrak{X}^*$ is continuous.

For the topological inclusion $X \subset \mathfrak{X}$ implies that the identical mapping of X^* into $\mathfrak{X}^*$ is closed (see [1], p. 41, th. 7), i. e. the set of all pairs (x, x) is closed in the Cartesian product $X^* \times \mathfrak{X}^*$.

Consequently, by (ix) and (iv) (for the method $\mathfrak{M}$),

(x) If $\mathfrak{M}$ is stronger than M , then $\tilde{f}$ is a continuous linear functional on X^* .

The following theorems on consistency follow immediately from (vii), (viii), (x).

(xi) Let x satisfy the hypotheses of (vii). If $\mathfrak{M}$ is stronger than M and $f(x_q) = \tilde{f}(x_q)$ for $q \in Q$, then $f(x) = \tilde{f}(x)$.

(xii) Suppose the hypotheses of (viii) are satisfied. If $\mathfrak{M}$ is stronger than M and $\lim_{q \rightarrow q_0} f(x_q) = \lim_{q \rightarrow q_0} \tilde{f}(x_q)$, $\lim_{q \rightarrow q_0} f(x_q^0) = \lim_{q \rightarrow q_0} \tilde{f}(x_q^0)$ and $f(x^0) = \tilde{f}(x^0)$, then $f(x) = \tilde{f}(x)$.

Examples. If X is the space of all sequences $x = \{\xi_n\}$ of real numbers, $P = Q =$ the set of all positive integers, $p_0 = q_0 = \infty$, $x_q = T_q(x) = \{\xi_1, \xi_2, \dots, \xi_q, 0, 0, 0, \dots\}$, and $f_p(x_q) = \sum_{k=1}^q a_{pk} \xi_k$ (where $A = \{a_{pk}\}$ is an infinite square matrix), then M is the Toeplitz method determined by the matrix A . It follows from (xii), where $x^0 = \{1, 1, 1, \dots\}$ (it follows from (xi)), that if M and $\mathfrak{M}$ are permanent (permanent for null sequences) and $\mathfrak{M}$ is stronger than M , then M and $\mathfrak{M}$ are consistent for bounded sequences (for bounded sequences summable by M to zero). This theorem is weaker than Theorem 2 (Theorem 1) of Mazur and Orlicz [3].

Similarly, if X, Q, q_0, x_q have the same meaning as in the above example, and if $P = \langle p_1, p_0 \rangle$ is an interval and $f_p(x_q) = \sum_{k=1}^q a_k(p) \xi_k$ (where $\{a_k(p)\}$ is a sequence of functions defined on P), then M is a function method examined recently by Włodarski ([5], [6]). Notice that our definition of the field X^* of the method M is different from that of Włodarski [5]. If the functions $a_k(p)$ satisfy the additional conditions of Włodarski [5] (definition 8), these definitions coincide. Włodarski's [5] Theorem X is a particular case of (xii).

Another example is the following one. Let $P = Q = \langle 0, \infty \rangle$, $p_0 = q_0 = \infty$, let X be the space of all functions $x = x(t)$ defined in $\langle 0, \infty \rangle$ and integrable in each finite interval $\langle 0, t_0 \rangle$, let x_q be the function: $x_q(t) = x(t)$ if $t \leq q$ and $x_q(t) = 0$ if $t > q$, and let

$$f_p(x_q) = \int_0^q K(p, t) x(t) dt$$

where $K(p, t)$ is a function on $P \times Q$, satisfying such conditions that (e

and (d) are true. The method M of this integral type has been but little examined in the general case.

The above generalization of the Mazur-Orlicz theory seems insufficient. In order to obtain by the above method the generalization of Theorems 1 and 2 of Mazur-Orlicz [3] (the consistency in the set of bounded sequences) it seems to be necessary to consider some linear non-metric spaces. Another generalization is necessary to obtain a general theory of summability of sequences of functions and, more generally, of sequences of elements of a Banach space (the functionals $f_{p,q}$ should then be replaced by linear operations).

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On the equation $x_1 x_2 \dots x_n = t^k$

by

A. SCHINZEL

Presented by W. SIERPIŃSKI on November 17, 1954

E. T. Bell has given (without proof) formulas for the general solution of the equation $x_1 x_2 \dots x_n = t^2$ in natural numbers $x_1, x_2, \dots, x_n, t$; the formulas contain $n(n+1)/2$ arbitrary parameters [1]. G. Browkin has raised the problem of finding, for given natural numbers n and k , all solutions in natural numbers $x_1, x_2, \dots, x_n, t$ of the equation

$$(1) \quad x_1 x_2 \dots x_n = t^k.$$

The solution of this problem is the object of the present note. It is to G. Browkin that I owe a certain simplification of the proof of the following theorem.

THEOREM. *Let n and k be given natural numbers and let*

$$(2) \quad \sum_{i=1}^n a_{j,i} = k \quad (j=1, 2, \dots, s)$$

*be all decompositions of number k into n non-negative integer components (decompositions differing in the order of their components being regarded as different) *).*

All solutions of equation (1) in natural numbers $x_1, x_2, \dots, x_n, t$, and only such solutions, are contained in the formulas

$$(3) \quad x_i = a_1^{a_{1,i}} a_2^{a_{2,i}} \dots a_s^{a_{s,i}} \quad (i=1, 2, \dots, n), \quad t = a_1 a_2 \dots a_s,$$

where $a_1, a_2, \dots, a_s$ are arbitrary natural numbers.

Proof. There is no difficulty in proving that if, for arbitrary natural $a_1, a_2, \dots, a_s$, we determine the numbers $x_1, x_2, \dots, x_n$ and t from formulas (3), then we shall obtain natural numbers satisfying equation (1). It remains to be proved that if $x_1, x_2, \dots, x_n, t$ are natural numbers satisfying equation (1), then there exist natural numbers $a_1, a_2, \dots, a_s$ for which formulas (3) hold.

*) As we know, $s = \binom{n+k-1}{k}$, see [2].

Let $x_1, x_2, \dots, x_n$ be natural numbers satisfying equation (1). Let us denote by a_1 the greatest natural number for which

$$(4) \quad a_1^{a_{1,i}} | x_i, \quad \text{for } i=1, 2, \dots, n.$$

Now let j denote a given natural number, $1 < j \leq s$, and suppose that we have already defined all numbers $a_1, a_2, \dots, a_{j-1}$ and that

$$(5) \quad a_1^{a_{1,i}} a_2^{a_{2,i}} \dots a_{j-1}^{a_{j-1,i}} | x_i, \quad \text{for } i=1, 2, \dots, n,$$

(which, by (4), is true for $j=2$). We shall define the number a_j as the greatest natural number for which

$$(6) \quad a_1^{a_{1,i}} a_2^{a_{2,i}} \dots a_{j-1}^{a_{j-1,i}} a_j^{a_{j,i}} | x_i, \quad \text{for } i=1, 2, \dots, n.$$

From (5) it follows that such a natural number $a_j \geq 1$ exists.

In this manner numbers a_j ($j=1, 2, \dots, s$) have been defined by induction, and for $j=1, 2, \dots, s$ we have formulas (6). Thus, numbers

$$(7) \quad y_i = x_i a_1^{a_{1,i}} a_2^{a_{2,i}} \dots a_s^{a_{s,i}} \quad (i=1, 2, \dots, n)$$

are natural. Hence, by (1) and (2),

$$(8) \quad y_1 y_2 \dots y_n a_1^k a_2^k \dots a_s^k = t^k.$$

Let p denote any prime number. For $i=1, 2, \dots, n$ let us denote by β_i the non-negative exponent with which number p enters into the expansion of number y_i into prime factors. Thus, into the expansion of the product $y_1 y_2 \dots y_n$ into prime factors, number p enters with the exponent $\beta_1 + \beta_2 + \dots + \beta_n$ and we infer from (8) that this sum must be divisible by k . Thus, if we had $\beta_1 + \beta_2 + \dots + \beta_n > 0$, then we should have $\beta_1 + \beta_2 + \dots + \beta_n \geq k$ and there would exist an integer r , $0 \leq r < n$, such that $\beta_1 + \beta_2 + \dots + \beta_r < k \leq \beta_1 + \beta_2 + \dots + \beta_{r+1}$ (where $\beta_1 + \dots + \beta_r$ should be taken to mean the number 0, if $r=0$). Let

$$\gamma_i = \begin{cases} \beta_i & \text{for } 1 \leq i \leq r \text{ (provided } r > 0) \\ k - (\beta_1 + \beta_2 + \dots + \beta_r), & \text{for } i = r+1 \\ 0 & \text{for } r+2 \leq i \leq n \text{ (provided } r < k-1). \end{cases}$$

It can easily be verified that $\beta_i \geq \gamma_i \geq 0$ for $i=1, 2, \dots, n$, and $\gamma_1 + \gamma_2 + \dots + \gamma_n = k$. Thus from the definition of numbers $a_{j,i}$ it follows that there exists a natural number $j \leq s$ such that $\gamma_i = a_{j,i}$ for $i=1, 2, \dots, n$.

In view of the definition of numbers β_i we have $p^{\beta_i} | y_i$, whence, by (7) and $a_{j,i} = \gamma_i \leq \beta_i$,

$$a_1^{a_{1,i}} a_2^{a_{2,i}} \dots a_{j-1}^{a_{j-1,i}} (p a_j^{a_{j,i}} | x_i, \quad \text{for } i=1, 2, \dots, n,$$

which contradicts the definition of the number a_j .

Therefore we must have $\beta_1 + \beta_2 + \dots + \beta_n = 0$, i. e. $\beta_i = 0$ for $i = 1, 2, \dots, n$. Thus no prime number p divides any of the numbers $y_i (i = 1, 2, \dots, n)$, whence it follows that $y_i = 1$ for $i = 1, 2, \dots, n$, and formulas (7) imply formulas (3) for $x_i (i = 1, 2, \dots, n)$, whence, by (1), we also have formula (3) for the number t .

Our theorem is proved.

Thus solutions (3) of equation (1) contain $\binom{n+k-1}{k}$ parameters.

E. g., for $n=2$, $k=3$ we have 4 decompositions of the number 3 into two non-negative integral components, namely $3=3+0=0+3==2+1=1+2$, whence we obtain $\alpha_{1,1}=3$, $\alpha_{1,2}=0$; $\alpha_{2,1}=0$, $\alpha_{2,2}=3$; $\alpha_{3,1}=2$, $\alpha_{3,2}=1$; $\alpha_{4,1}=1$, $\alpha_{4,2}=2$, which implies that the solutions of the equation $x_1 x_2 = t^3$ in natural numbers x_1, x_2, t are

$$x_1 = a_1^3 a_3^2 a_4, \quad x_2 = a_2^3 a_3 a_4^2, \quad t = a_1 a_2 a_3 a_4$$

(where a_1, a_2, a_3, a_4 are arbitrary natural numbers); these formulas have been obtained by W. Sierpiński in a different way.

For $n=4$, $k=2$ we have, in view of $\binom{5}{2}=10$, 10 decompositions of the number 2 into the sum of 4 non-negative integers, which gives ten-parameter formulas for the solutions in natural numbers x_1, x_2, x_3, x_4, t of the equation $x_1 x_2 x_3 x_4 = t^2$, coinciding with the formulas given by E. T. Bell in the work cited above.

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A possible example of decay in flight of a charged hyperon

by

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In a nuclear emulsion (G5 600 μ), exposed at high altitude, we observed an event which may be interpreted as decay in flight of a single-charged particle of hyperprotonic mass.

One of the secondaries from a star of the type $18+11p$ after 2590 μ (track 1 in Fig. 1) changes the direction of its motion through an angle

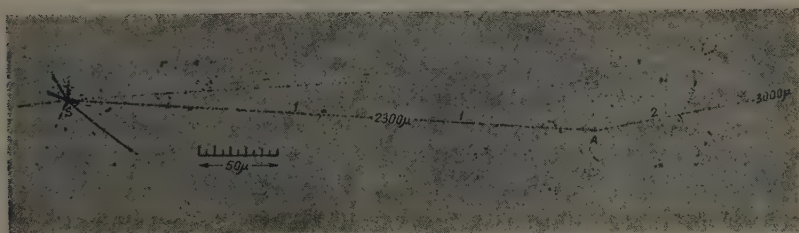


Fig. 1

of $(22 \pm 1)^\circ$ and after running another 3000 μ (track 2) enters the glass. The change in the direction of motion is accompanied by a sudden decrease in grain density. Grain counting made along tracks 1 and 2 yields respectively:

$$g_1 = (66 \pm 4) \text{ grains per } 50 \mu,$$

$$g_2 = (44 \pm 3) \text{ grains per } 50 \mu,$$

showing no abnormal changes in grain density along each of the tracks. The limits of error given above are about four times larger than those of purely statistical errors and correspond to the estimated accuracy of grain counting on such high grain density tracks. Moreover, as the plate shows a satisfactory uniformity of development, the difference in

grain density observed between the two tracks can be considered as a significant one.

Multiple scattering measurements made along these two tracks yield respectively:

$$\bar{\alpha}_1 = (0.21 \pm 0.03) \text{ degrees per } 100 \mu,$$

$$\bar{\alpha}_2 = (0.10 \pm 0.015) \text{ degrees per } 100 \mu,$$

with errors calculated according to the convention $\Delta\bar{\alpha} = 0.6/\sqrt{m}$, where m is the number of independent cells.

From measurements made along three proton tracks ($R \sim 30$ mm.) and two π -meson tracks ($R \sim 10$ mm.) ending in the emulsion, a range vs. grain density relation was obtained. From these results a calibration curve grain density vs. momentum $\times$ velocity was calculated using extrapolated range-energy relation [1, 2, 3]. The accuracy as regards the grain density of this relation is estimated to be the same as that of the grain density measurements for tracks 1 and 2.

Using these data, we obtain for the masses of particles 1 and 2:

$$m_1 = \left(\begin{matrix} 1930 & +670 \\ & -490 \end{matrix} \right) m_e$$

$$m_2 = \left(\begin{matrix} 2160 & +650 \\ & -500 \end{matrix} \right) m_e.$$

The marked and significant decrease in grain density rules out the possibility of considering the event as due to large-angle scattering.

Mass evaluation indicates that particle 1 is considerably lighter than a deuteron, whereas particle 2 is considerably heavier than a π -meson.

If the possibility of particle 1 being a deuteron is ruled out, it seems likely that we are dealing with a decay in flight of an unstable particle with the emission of one charged particle of about protonic mass.

Tentatively assuming particle 1 to be a hyperon decaying according to the scheme:

$$\Omega^+ \rightarrow p + \pi^0,$$

the calculated Q -value of the decay is:

$$Q_\Omega = \left(\begin{matrix} 140 & +40 \\ & -30 \end{matrix} \right) \text{ MeV}$$

and the mass of the hyperon:

$$M_\Omega = \left(\begin{matrix} 2370 & +80 \\ & -60 \end{matrix} \right) m_e,$$

the time of flight of particle 1 being 3×10^{-11} sec.

From among 19 grey and minimum tracks of the primary star only 4 may be identified: two are protons and 2 are light mesons. So our measurements give no information about the possible emission of a heavy meson here.

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Possible example of decay of a “meson active triton” at rest

by

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A stack of Ilford G5 plates, 600μ thick, flown at an altitude of about 25.000 m. during 6.5 hours, were systematically scanned for double stars interconnected by heavily ionising particle tracks.

Among some 100 double stars of this type, one showed features remarkably similar to the cases of decay of a “meson active triton” at rest, described by Bonetti et al. [1] and by Debenedetti et al. [2].

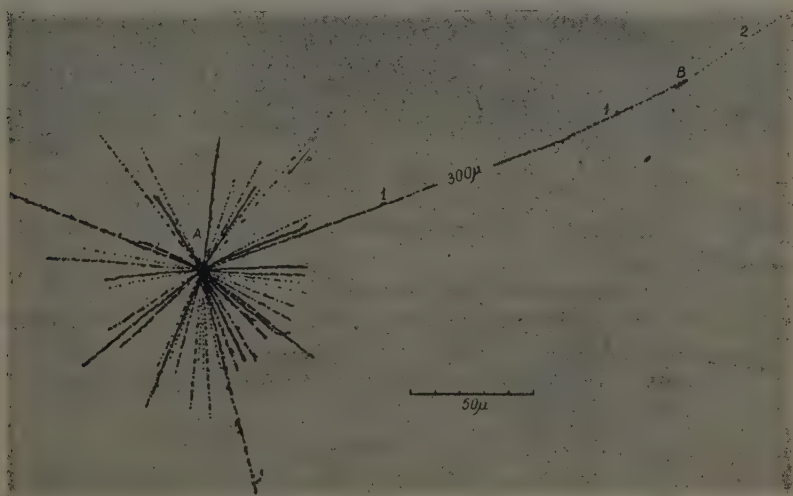


Fig. 1

Since an account of the systematic analysis of all these double stars is to be published later elsewhere — only a brief description of the data concerning this special event will be given here.

A drawing of this event is shown in Figs. 1 and 2.

From a star (*A*) of the type $37+7p$ there emerges a black track (*f*) which ends in the emulsion in a two-prong star (*B*). Track *f* seems to be due to a heavy, single-charged particle, stopping, or nearly stopping, at point *B*, as on its whole length of 520μ only one δ -ray is observed. Assuming particle *f* to be stopped in the emulsion, a rough estimate of its mass from the $\bar{a}-R$ measurements, using the constant sagitta method, yields: $m_f \sim 2.7 m_p$.

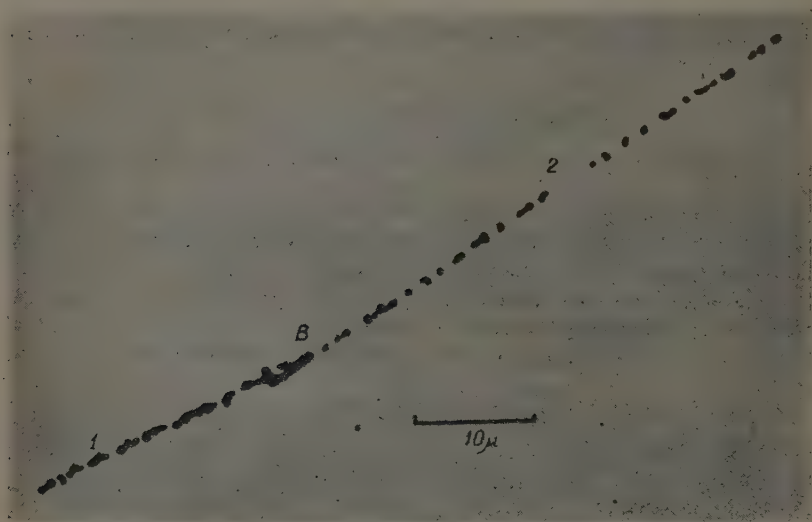


Fig. 2

These data suggest that we have to do here with a particle heavier than a proton which is a triton rather than a deuteron and that it is a slow particle near the end of its range.

The secondaries of star *B* are, within the limits of error, ejected in opposite directions.

Track 1 is 9.9μ long. Assuming it to be due to a ${}^3\text{He}$ nucleus, one finds for its kinetic energy:

$$E_{{}^3\text{He}} = (2.6 \pm 0.6) \text{ MeV } ^*).$$

After 290μ track 2 leaves the emulsion. It can be identified, however, in the facing plate and followed for a further 760μ . Scattering and grain density measurements made on this track give a rough indication as to the mass of particle 2: $m_2 \sim 400 m_e$.

*) According to the data of Catala et al [4] and Rotblat [3] with a 3.5% correction in stopping power for humidity content in the emulsion.

The measurements here suggest a light meson. Assuming particle 2 to be a π -meson, one finds from the grain density on its track that the value of its kinetic energy is:

$$E_{\pi} = (50 \pm 15) \text{ MeV.}$$

All these data taken separately from the cases of Bonetti et al. and Debenedetti et al. may lead to similar conclusions but with less convincing arguments. Comparing them, however, we find that the excellent agreement in all detectable features seems to give very strong support to the conclusion that we have here to do with identical processes uniquely defined as concerns the masses, charges and momenta of the particles involved. In other words, that we have here to do with the same two-body decay of an unstable particle at rest.

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The influence of fatty acids on the polarisation curves of iron in ammonium nitrate

by

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Presented by M. ŚMIAŁOWSKI on October 18, 1954

In an earlier paper [1] it was stated that the greater the length of the hydrocarbon chain of a molecule of fatty acid added to the corroding medium, the slower is the rate of stress corrosion of mild steel in ammonium nitrate solution. Since the corrosion of iron in ammonium nitrate is an electrochemical process (a fact which was proved incontestably by, among others, Waber and McDonald [2]), it seemed appropriate to undertake experiments to find whether fatty acids influence the rate of the cathodic or of the anodic reaction. The experiments consisted in plotting the course of polarisation curves in solutions of ammonium nitrate with additions of various fatty acids.

All the measurements were taken on one and the same plate of mild steel with a content of 0.09% C. The plate formed the bottom of one of the arms of an H-shaped glass vessel, with a capacity of 15 ml., to which it was stuck by means of a special glue resistant to the action of nitrate. In the other arm was a platinum plate which served as an auxiliary electrode of the cell. Both arms of the vessel were open at the top. Through the opening above the steel electrode under examination was inserted a capillary tube, of which the lower outlet was just above the surface of the metal; this capillary tube, filled with a KNO_3 solution, connected the electrolytic cell through a 5 N KNO_3 salt bridge with a saturated calomel electrode. Before each experiment the steel plate was etched with diluted sulphuric acid and dried for an hour at a temperature of 70° C. Before the measuring, there was poured into the vessel 12 ml. of a 5 N ammonium nitrate solution, or the same with the addition of a suitable quantity of a freshly prepared solution of fatty acid in methanol; first the established static potential of the steel plate was measured and then polarisation was commenced. Measurements of the potentials, with accuracy up to 2 mV., were taken at room temperature with the aid of a valve potentiometer.

The static potential in relation to the saturated calomel electrode established itself in the conditions described with relatively good reproducibility at a value within the range of from -0.57 to -0.58 volts. In the presence of the additional substances satisfactory reproducibility of the results was obtained for the series of normal fatty acids ranging from $C_4H_8O_2$ (*n*-butyric acid) to $C_{18}H_{36}O_2$ (*n*-pelargonic acid). The curves of cathodic polarisation were plotted as the current density gradually decreased, whereas the plotting of the curves of anodic polarisation took

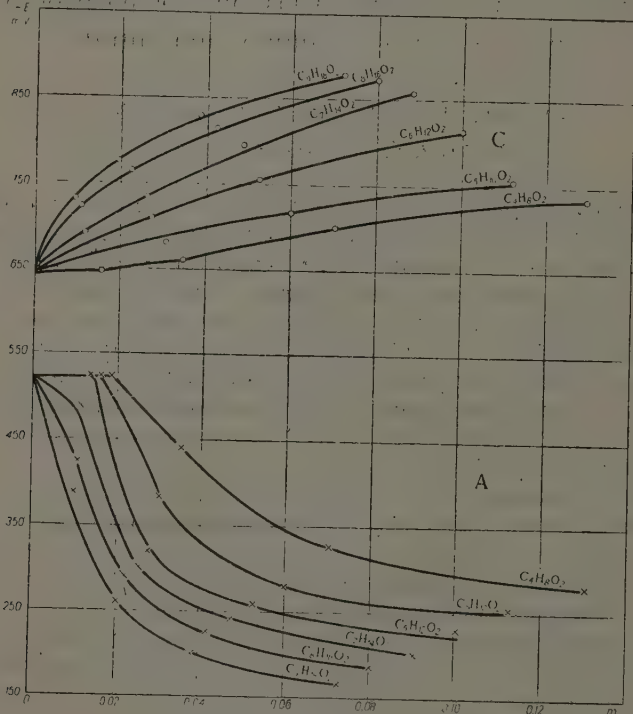


Fig. 1

place as the current density gradually increased. The reproducibility of the curves of cathodic polarisation was better than that of the curves of anodic polarisation. In the case of the latter, beyond a certain limit of current density, there occurred a marked jump of the potential towards the positive values. This jump, caused by the passivation of the steel, took place in the presence of fatty acids at a lesser current density than in the pure NH_4NO_3 solution.

Fig. 1 shows curves representing the dependence of the potential ($-E$ in millivolts) of an iron electrode in relation to a saturated calomel

electrode on the quantity (m in mols per litre) of the different fatty acids added to the 5 N NH_4NO_3 solution, when there is a constant polarising current density equal to $6.6 \cdot 10^{-4}$ amp./cm². As can be seen, the addition of fatty acid influences the course of the curves of both anodic (A) and cathodic (C) polarisation to a degree depending on the length of the hydrocarbon chain of the molecule.

In Fig. 2 were presented, in function of the number n of carbon atoms in a molecule of normal fatty acid, the absolute values of the changes produced in the potentials of a working anode and cathode ($|\Delta E|$ in millivolts) by the addition of different fatty acids to a 5N solution of NH_4NO_3 ; the quantity of the additions used in these experiments was always the same and amounted to

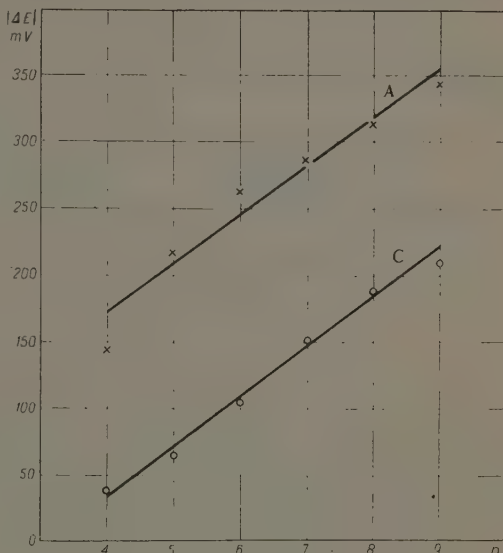


Fig. 2

0.05 mols per litre, while the current density was equal to $6.6 \cdot 10^{-4}$ amp./cm².

It can be seen from this diagram that the changes produced in the potential by the various additions of fatty acids are somewhat greater in the case of polarisation of an iron anode than in the case of polarisation of an iron cathode. In both cases the dependence of ΔE on n is approximately linear.

Summary

Plotting of the polarisation curves of iron in a 5 N solution of ammonium nitrate in the presence of different normal fatty acids, ranging from $\text{C}_4\text{H}_8\text{O}_2$ to $\text{C}_9\text{H}_{18}\text{O}_2$, showed that additions of these compounds influence polarisation both of the anode and of the cathode, although to a lesser degree in the case of the latter. The extent of this influence depends on the number of carbon atoms in a molecule of fatty acid. The presence of fatty acids facilitates the passivation of iron anodes in an NH_4NO_3 solution.

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Cryometric investigation of fractions obtained by fractional distillation of 2-picoline

by

W. ŚWIĘTOSŁAWSKI and R. CIECHOMSKA

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of December 13, 1954

1. Introductory remarks

Some years ago Coulson and Jones [1] described the phenomena taking place when pyridine bases are submitted to a fractional distillation on an effective distilling column. Under these conditions relatively large intermediate fractions are obtained without any sharp transition separating the pyridine, 2-picoline and so-called three-degree fraction 142-145°C. levels on the distilling curve. On the other hand, W. Glowacki [2] determined the most important physical properties of a pure 2-picoline sample, but made no mention of the difficulties to be encountered in preparing the pure base under consideration. For this reason it seemed important to examine, by means of the cryometric method, the fractions collected in the course of a fractional distillation of a 2-picoline fraction obtained from a technical product on a large-scale batch distilling column.

2. Cryometric examination of pyridine bases

It was shown in previous papers [3], [4], [5] that a suitable method for examining pyridine bases and their mixtures consists in a cryometric examination of dehydrated hydrochlorides.

A sample of the pyridine base is treated with hydrochloric acid and brought to the boil, and then the excess of hydrochloric acid is easily removed with water vapour. The hydrochloride salts of all the pyridine bases boil at temperatures exceeding 200°C. Because of that, there is no difficulty in proving that the removal of water and hydrogen chloride is a quantitative one. Experiments [3] have shown, however, that the samples of any of the hydrochlorides thus obtained contain an excess of hydrogen chloride. This is the only disadvantage of the method, because, owing to this excess, the freezing temperature of the melted hydrochloride decreases with an increase in the amount of the solid phase.

In our experiments we determined three equilibrium temperatures: t_1 , $t_{1/2}$ and t_2 , where t_1 is the temperature at which the last crystals disappear, t_2 — that at which from 80 to 90% of the hydrochloride becomes solidified, and $t_{1/2}$ corresponds to a state in which one half of the sample is in the solid and the other half in the liquid phase. For simplification, only t_1 , the temperature at which the crystals disappear, will be considered in this paper.

3. Cryometric measurements of forerunnings: main and end-fractions

It should be emphasized that technically pure 2-picoline fractions usually contain appreciable amounts of pyridine, 3-picoline, 4-picoline and 2,6-lutidine. Among these bases 2-picoline is characterized by the lowest value of t_1 . Below t_1 the values are given for all of the pyridine bases mentioned above.

Hydrochlorides	$t_1^{\circ}\text{C}$	3-Picoline	85
Pyridine	137.5	4-Picoline	161
2-Picoline	78	2,6-Lutidine	238

Because of the large difference in the freezing temperatures of pyridine and 2,6-lutidine, the former precipitates in the forerunnings and the latter in the end fractions of the batch distillation of technically pure 2-picoline. For this reason, when experimenting with the hydrochlorides, we must bear in mind that the above-mentioned contaminants should be called "main components" in the fractions collected at the beginning and at the end of the distillation. This is due also to the fact that the pyridine base hydrochlorides form eutectics with one another.

On the other hand, the middle fractions after being transformed into hydrochlorides, contain such an excess of 2-picoline that the precipitating crystals of the melted hydrochloride salts contain practically pure 2-picoline hydrochloride.

On the basis of the facts mentioned above, it is easy to conclude that in the forerunnings as well as in the end fractions two samples have to be found which, after being transformed into hydrochlorides, should each be characterized by a certain minimum "freezing" temperature.

The composition of these two samples should correspond or approximate closely to the composition of the two eutectics. The first minimum indicates that the composition of the sample is very similar to that of the eutectic pyridine-2-picoline hydrochlorides, and the second that of the eutectic of 2-picoline-2,6-lutidine hydrochloric salts. Thus the two fractions showing the minimum freezing temperatures of the hydrochlorides divide the distillation curve into three sections. In the first of these, pyridine hydrochloride is the main component, in the second, 2-picoline hydrochloride, and in the third, 2,6-lutidine. Consequently, when preparing a pure 2-picoline sample, the middle fraction

only should be used for further recrystallization of the hydrochloric salt from the free base.

It should be pointed out that similar phenomena can be observed in all cases in which an intermediate fraction separates the two others which correspond to two chemically pure compounds collected in the receiver. These two substances should form with each other an ideal binary eutectic.

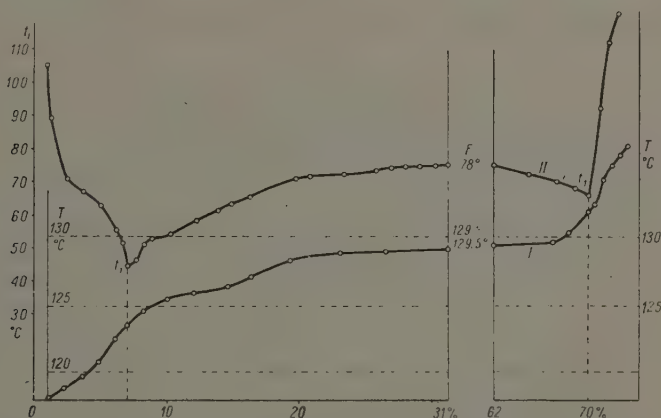


Fig. 1. Distillation curve I of a technically pure 2-picoline fraction. Curve II shows the temperature changes, corresponding to the disappearance of crystals in the melted hydrochloric salts. Temperatures t_1 and t'_1 correspond to the two minimum "freezing" temperatures indicating the existence of two eutectics: pyridine-2-picoline and 2-picoline-2,6-lutidine hydrochlorides, respectively. The main fraction F was collected within 129.0-129.5°C. Its "freezing" temperature was constant and equal to 78°C. Fraction F was collected within limits ranging from 31 to 62%. This part of the drawing was omitted in order to shorten the length of the figure.

It was stressed above that the temperature of the disappearance of crystals and not the "freezing" temperature was measured in our experiments. This was due to the supercooling phenomena which often take place not only in the case of pyridine base hydrochlorides, but in many other cases as well.

The physical properties of the fraction of 2-picoline collected within 129.0-129.5°C. did not differ from those described by Glowacki [2].

Summary

1. A batch distillation of a technically pure 2-picoline may be combined with a cryometric investigation of the fractions after their transformation into hydrochlorides. The removal of water and hydrochloric acid is an essay operation.

2. The curve showing the change in temperature at which the disappearance of crystals in the melted hydrochloride takes place is composed of three sections. In the

first, pyridine hydrochloride is the main component; in the second, 2-picoline hydrochloride precipitates first; in the third, 2,6-lutidine salt is the main component of crystallization. The three sections are divided from each other by hydrochlorides which show minima t_1 and t'_1 corresponding to the disappearance of crystals. These minima show the formation of two binary eutectics. The first (t_1) corresponds to the eutectic: pyridine-2-picoline hydrochloride, the second (t'_1) to the system: 2-picoline-2,6-lutidine hydrochlorides.

3. There is no evidence that pyrol is present in the technical 2-picoline fraction used in this investigation.

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The anodic behaviour of lead in phosphoric acid solutions

by

J. KAMECKI, Z. ZEMBURA, J. TRAU

Presented by B. KAMIENSKI on October 22, 1954

The anodic behaviour of lead has several times been the subject of research; this research has been concerned, among other things, with the processes taking place in accumulators [1], the theory of anodic passivation elaborated by Müller [2] and the behaviour of lead anodes in industrial galvanizing processes [3]. In these investigations, solutions of sulphuric acid were chiefly used, then saturated solutions of lead perchlorate, and solutions of chromic salts and of sodium hydroxide. Elbs and Nüblieng [4] carried out the electrolysis of phosphoric acid, of a specific gravity of 1.70 and 1.02, using lead anodes for preparative purposes.

The present paper describes investigations which were carried out in solutions of phosphoric acid, using the method previously described for the investigation of the anodic behaviour of copper [5] and zinc [6].

Plates of fire-refined rolled lead (content 99.51% Pb) $20 \times 30 \times 1$ mm. in size were used for the measurements, as well as plates of the same lead but galvanically coated with lead from a solution of fluoroborate. Two lead cathodes, $65 \times 60 \times 1$ mm. in size, were placed on both sides of the anode at a distance of about 5 cm. Before measurement, the anodes were degreased with benzene, etched with nitric acid (1:1), washed in water, dried in a current of hot air, and, immediately before measurement, were cleansed of oxidic deposits with a brass wire brush. The measurements were taken in solutions of 40.50, 22.80, and 2.99 N H_3PO_4 . These concentrations corresponded respectively to the following specific electric conductivities: 0.0920, 0.1990 and $0.0535 \text{ cm.}^{-1} \Omega^{-1}$.

The apparatus used for the measurements (Fig. 1) differed from that previously used as regards the position of the voltmeter and the ammeter. This was changed because in the former arrangement, as a result of the passivation of the lead during electrolysis, the voltmeter acted as a shunt and so the indications of the ammeter were not a direct measurement of the intensity of the current flowing through the electrolyser. In Fig. 1, Ak denotes the battery of accumulators, V — the voltmeter, A — the

ammeter, P — the potentiometer, E — the standard calomel electrode with saturated KCl solution, R_1 to R_4 — the rheostats with maximum resistances of 8250, 2000, 480 and 56 ohms.

Measurement of the ratio of anodic current density and of anodic potential to voltage applied to the cathode and anode was made at a temperature of $20 \pm 1^\circ\text{C}$ after the establishment of a stationary state. This required as a rule unchanged conditions for a period of time lasting from

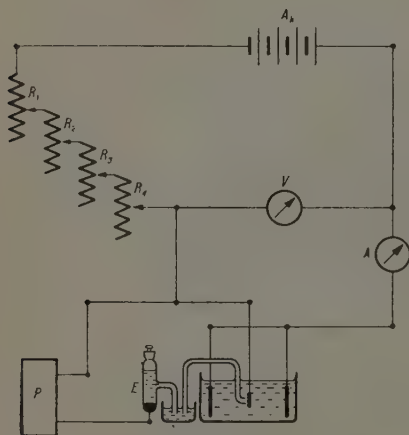


Fig. 1. Diagram of the apparatus for measuring the ratio of anodic current density and of anodic potential to electrolysis voltage.

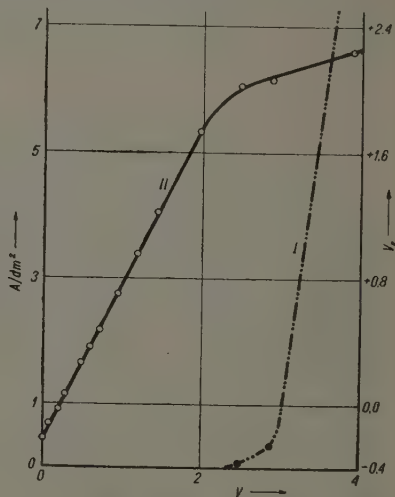


Fig. 2. Curves showing the ratio of anodic current density (I) and of anodic potential (II) to the voltage in a solution of 22.80 N H_3PO_4 .

about 30 to 60 minutes, and, in cases of sudden deflections in the curves, even 3 hours. Conformity of the measurements was better in the case of electrolytic lead than in that of fire-refined lead, and also when the solutions were more dilute. The results of the measurements of the anodic potentials with respect to the calomel electrode with saturated KCl solution were calculated in values with reference to a standard hydrogen electrode.

The curves representing the ratio of current density and of anodic potential to voltage are similar for all the solutions investigated. The curves on Fig. 2 are given as an example. On account of the size of the scale, it was not possible to show, in graph 2, the small but characteristic changes in the current density in the region from 0 to 2.5 V. These have been shown for all electrolytes in graphs 3 and 4.

Concurrently with these measurements, observations were made of changes in the appearance of the lead anode during electrolysis. These

changes were similar in the 3 solutions used, and took place in the same order. After immersion in the solution of phosphoric acid, but before the beginning of electrolysis, the lead plates became covered with a thin white coating. This coating darkened after the voltage exceeded 0.5 V and became brownish after it exceeded 0.8–1.2 V (depending upon the concentration). Independently of the concentration of the acid, the course of the curves representing the ratio of anodic current density to voltage was, on the whole, similar to the course observed previously in the case of copper or zinc in phosphoric acid, but on account of the ease of passivation of lead anodes, current density for voltages lower than 2 V is small and requires sensitive instruments if it is to be measured (Figs. 3 and 4).

On the basis of the measurements and observations described, the following course of reaction should be accepted: 1) in the first phase of electrolysis, regulated by the voltage (up to 0.5 V), the lead passes into solution (in solutions of 22.80 and 40.50 N a white deposit of plumbeous compounds rapidly appeared during electrolysis), and at the same time there is a weak residual current. At the same time the rise appearing in the anodic potential (from -0.24 to $+0.25$ V) indicates that, in proportion to the rise in voltage, the anode undergoes increasing passivation. This is probably caused by the coating of plumbeous phosphates which grows on the anode and becomes compact; 2) in the second phase, after exceeding a voltage of 0.5 V and in proportion to its further increase up to 0.85 and 1.2 V, the density of the current rapidly rises until it attains the maximum, which is not very great. At the same time the anodic potential increases at the same rate as before; this is signaled by an intensification of the passive state of the anode. Meanwhile the anode darkens, a fact which seems to indicate that it has become coated with lead oxide. It is possible that this is a result of the reaction: $\text{Pb} + 2\text{OH}^- = \text{PbO} + \text{H}_2\text{O} + 2e$. From the moment of exceeding the maximum there follows, as a result of increasing passivation, another fall

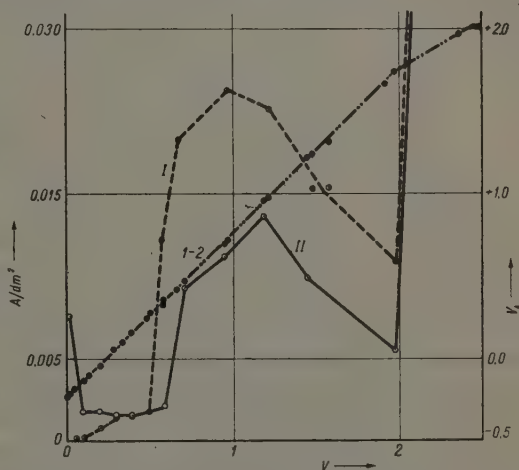


Fig. 3. Graph showing the ratio of anodic current density (I and II) and of anodic potential (1 and 2) to voltage in solutions of 2.99 N (curves I and 1) and 22.80 N H_3PO_4 (curves II and 2).

in current intensity. It is possible that at the same time PbO_2 begins to form in the reaction $\text{Pb} + 4\text{OH}^- = \text{PbO}_2 + 2\text{H}_2\text{O} + 4e$ or through the

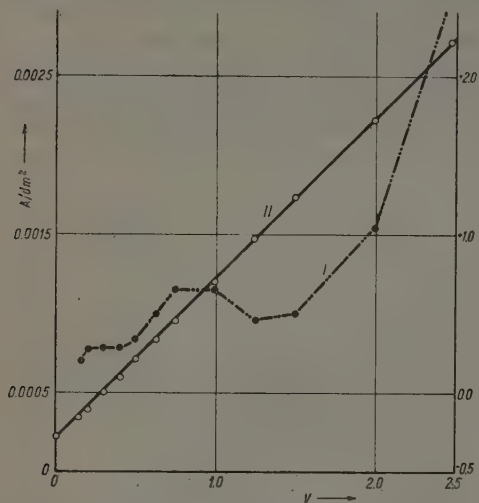


Fig. 4. Graph showing the ratio of anodic current density (I) and of anodic potential (II) to voltage in a solution of 40.50 N H_3PO_4 .

phosphoric acid, which in the conditions described amounts to c. 2 V with anodic potentials of +1.75, +1.88 and +1.93 V in solutions of 2.99, 22.80 and 40.50 N H_3PO_4 respectively.

oxidation of PbO . Passivation is practically ended from the moment of applying a voltage of 2.2, 3, and 2.2 V in solutions of 2.99, 22.80 and 40.50 N H_3PO_4 respectively. The anodic potential then amounts respectively to +2.0, +1.96 and +2.2 V, and increases but little with a further raising of the voltage. On the other hand, anodic current density begins to increase rapidly, especially with voltages exceeding 2.86, 2.88 or 3.04 V, and at the same time a brisk liberation of oxygen begins on the anode. This doubtless follows as a result of exceeding the decomposition voltage of phos-

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The passivation of lead anodes in phosphoric acid solutions

by

J. KAMECKI, Z. ZEMBURA and J. TRAU

Presented by B. KAMIENSKI on October 22, 1954

In the preceding paper [1] we ascertained on the basis of measurements of the ratio of anodic current density and of anodic potential of lead to electrolysis voltage in solutions of phosphoric acid, that the passivation of lead anodes proceeds with ease, and we gave the probable course of the reaction. In the present paper the results are given of further investigations into the course of the passivation of lead anodes in 2.99, 22.80 and 40.50 N H_3PO_4 solutions. The measurements consisted in determining the ratio of anodic potential to time, using a current of constant density. The apparatus used for the measurements and the method used for preparing the samples have both been described in a previous paper [1]. On the basis of a few score series of measurements (on account of the difficulty of reproducing the results) made at various current densities, the characteristic shape of the curves representing the ratio of anodic potential to time was established. Some of these curves are presented in Fig. 1 (2.99 N solution), in Fig. 2 (22.80 N solution), and in Fig. 3 (40.50 N solution). The results obtained in 2.99 and 40.50 N solutions were not dependent on the kind of lead used (fire-refined rolled or electrolytic), whereas in the 22.80 N solution differences were noted.

All curves representing the ratio of anodic potential to time at a constant current density showed clearly marked maxima. The time required to reach the maximum we call the "passivation time" and have denoted it by the symbol t_p . The anodic current density (expressed as $A/dm.^2$) multiplied by the passivation time t_p in seconds gives the amount of electricity F_p in coulombs necessary for the passivation of an anode $1 dm.^2$ in area. Both t_p and F_p are defined as functions of the anodic current density of polarization, which is the same for all solutions. In Fig. 4 are given, by way of example, the curves representing the ratio of t_p and $1/t_p$ to anodic current density in a solution of 2.99 N H_3PO_4 .

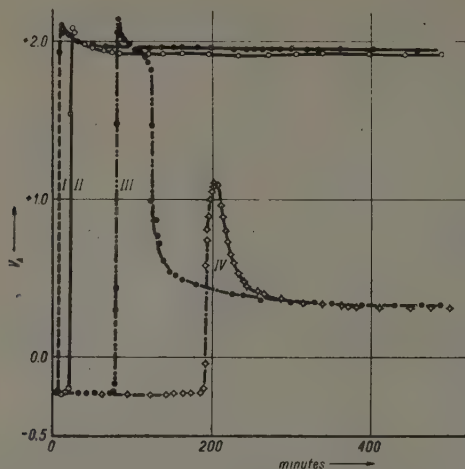


Fig. 1. Curves representing the ratio of anodic potential to time of electrolysis in minutes at constant anodic densities of 0.0730 (curve I), 0.0365 (II), 0.0146 (III), and 0.00755 A/dm^2 (IV) in solutions of 2.99 N H_3PO_4 .

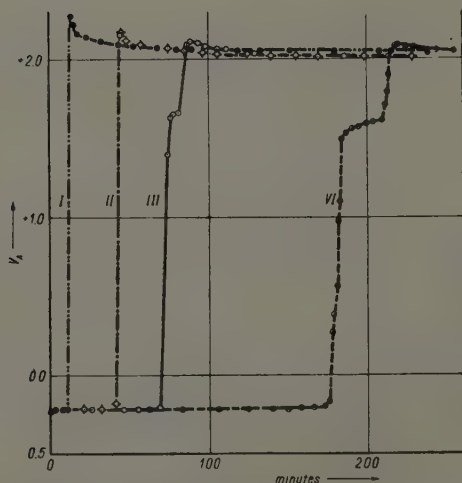


Fig. 2. Curves representing the ratio of anodic potential to time of electrolysis at constant anodic current densities of 0.0499 (I), 0.0152 (II), 0.0100 (III), and 0.00513 A/dm^2 (IV) in 22.80 N H_3PO_4 (electrolytic lead)

It can be seen from the graph in Fig. 4 that the curves representing the ratio of $1/t_p$ to anodic density D approximate to straight lines except that in a solution of 40.50 N the curve should be broken into two straight sections. With the help of the method of least squares it has been found that in a 2.99 N solution

$$1/t_p = 1.58D - 0.008 \text{ i. e. } t_p = \frac{1}{1.58D - 0.008};$$

for fire-refined lead in a 22.80 N solution

$$t_p = \frac{1}{1.31D - 0.007};$$

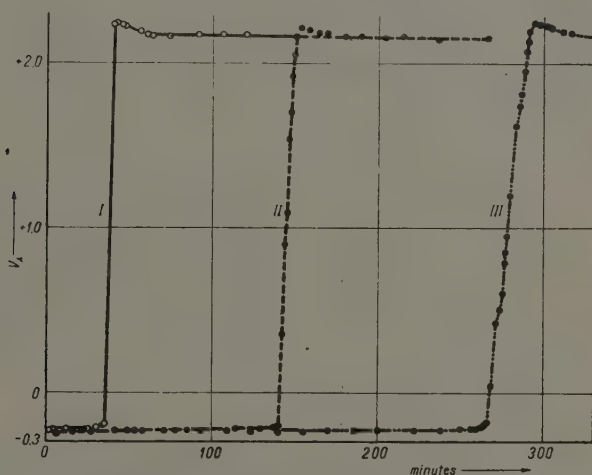


Fig. 3. Curves representing the ratio of anodic potential to time of electrolysis at constant anodic current densities of 0.300 (I), 0.00993 (II), and 0.00506 A/dm^2 . (III) in 40.50 $N H_3PO_4$.

for electrolytic lead in a solution of the same composition:

$$t_p = \frac{1}{1.14D - 0.0015};$$

finally, for densities less than 0.03 A/dm^2 in a 40.5 N solution

$$t_p = \frac{1}{0.83D - 0.0016};$$

and for densities greater than 0.03 A/dm^2 .

$$t_p = \frac{1}{2.57D - 0.05}.$$

The amount of electricity F_p required for the passivation of an anode 1 dm.² in area is calculated by multiplying the previously obtained expression for t_p by 60 D .

The above expressions for t_p and F_p have the general form:

$$t_p = \frac{1}{aD - b} \quad \text{and} \quad F_p = \frac{60D}{aD - b}.$$

For high densities b can be neglected because of its low value. Then we have approximately:

$$t_p = \frac{1}{aD} \quad \text{and} \quad F_p = \frac{60D}{aD} = \frac{60}{a},$$

while for high anodic densities the passivation time t_p is in inverse proportion to the anodic density, and amounts of electricity required for the passivation of a unit of area of an anode (in this case 1 dm.².) are constant and not dependent on the density. The influence of the quality of the lead on passivation could be observed only in the 22.80 N solution, i. e., in the solution with the greatest conductivity.

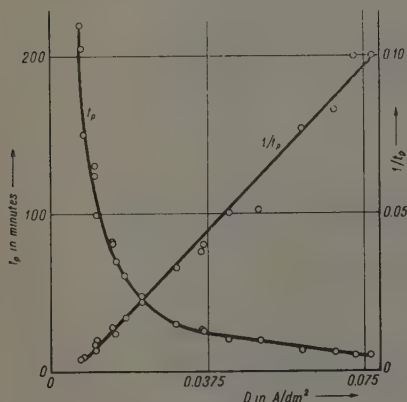


Fig. 4. Curves representing the ratio of passivation time t_p and the reverse of passivation time $1/t_p$ to anodic current density in a 2.99 N solution of H_3PO_4 .

By decreasing the intensity of the current, we reach the limit value of current density D_g at which, in spite of the arbitrary length of time of electrolysis, passivation does not take place. The limit value of the current density is then:

$$D_g = \frac{b}{a},$$

and for solutions of 2.99, 22.80 and 40.50 N H_3PO_4 it amounts respectively to 0.0043, 0.0053 (fire-refined lead), 0.0013 (electrolytic lead), and 0.0019 A/dm^2 .

The course of dependence of the anodic potential on time at a constant anodic density is similar in the majority of cases. Initially this potential remains low (e. -0.22 to -0.24 V), which corresponds to the transition of the lead as Pb^{++} into a solution of low Pb^{++} ion concentration (e. g. the potential of lead in the case of the reaction $Pb + 2Cl^- = PbCl_2 + 2e$ amounts to -0.268 V, while the normal potential of lead amounts to -0.126 V). After a certain period of time, the lower the current density the longer the time, there follows a sudden jump in the anodic potential to values ranging from +2.06 to +2.25 V; this is a result of the coating of the anode with the products of electrolysis, which, according to

Müller, causes a decrease in the free pores for the current and an increase in the intensity of the current in these pores, leading to a high passivity of the anode. The anode then becomes coated with PbO_2 . Since PbO_2 is a conductor of electric current, the resistance of the system diminishes in proportion to coating the anode with PbO_2 , and for the maintenance of a constant density it is necessary to lower the electrolysis voltage. As a consequence of this the anodic potential drops a little to a stationary value ranging from $+1.96$ to $+2.16$ V (the lowest value is obtained in a 22.80 *N* solution).

In more concentrated solutions, before reaching the maximal passivity, two more or less clearly marked stationary points appear on the curves representing the ratio of anodic potential to time; the first of these corresponds to an anodic potential of c. $+0.3$ V, the second, to one of from $+1.4$ to $+1.6$ V. It is possible that the first corresponds to the coating of the anode with PbO , and the second to the initial formation of PbO_2 , in agreement with the reaction $\text{PbO} + 2\text{OH}^- = \text{PbO}_2 + \text{H}_2\text{O} + 2e$ or under the influence of the action of the free OH radicals arising from the anodic reaction $\text{OH}^- = \text{OH} + e$ (normal potential $+1.4$ V). We remarked on the possibility of this kind of reaction in a previous paper [2] (zinc in KOH). Krasilshchikov [3] also puts forward this possibility in the case of the anodic behaviour of nickel.

Still more complicated relations arise in the case of a 2.99 *N* solution (Fig. 1). For high densities, the course of dependence of potential on time is similar to that described above. For lower densities, however, after the maximum (c. $+2$ V) has been attained, a drop to a stationary value of c. $+0.3$ to $+0.4$ V follows. At still lower densities the anodic potential does not attain the value of $+2$ V at all, but a markedly lower value, and then falls again to a value of from c. $+0.3$ to $+0.4$. The proper interpretation of these phenomena requires a knowledge of the composition of the coating on the anode.

Since the normal potential of the reaction $\text{Pb}^{4+} + 2e = \text{Pb}^{2+}$ has a value of $+1.69$ V, while that measured for the maximum amounts to c. $+2$ V, we assume (by analogy with the behaviour of lead in H_2SO_4), that in these conditions there takes place on the anode the reaction of formation of plumbic phosphate, which only then undergoes hydrolysis into PbO_2 .

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On the azeotropic range of acetic acid with respect to the homologous series of paraffin hydrocarbons

by

Z. KURTYKA

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of December 13, 1954

1. Introductory remarks

A method for determining the azeotropic ranges of a certain agent A with respect to hydrocarbons has been described by W. Świątosławski and A. Orszagh [1]. This method consists in using some fractions of gasoline, boiling within such a temperature range as to have the lowest H_c and the highest H_k representatives forming with agent A tangent, or almost tangent, boiling temperature isobars. It is not possible with this method to determine the shape of the isobars formed by A with each of the representatives of series (H).

Having in view the determination of one point only on the isobar, corresponding to the boiling temperature and to the composition of each individual azeotrope, a large majority of investigators have used exclusively the fractional distillation method [2]—[6].

In the present investigation acetic acid was chosen as the azeotropic agent because of the large azeotropic range of this substance with respect to normal paraffins. The purpose of these investigations was to determine, by means of the ebulliometric method, the composition of the azeotropes and also the shape of the boiling temperature isobars formed by the acetic acid with each of the normal paraffin hydrocarbons.

Further details concerning this investigation as well as those relating to purification, analysis and the technique of the ebulliometric measurements will be described elsewhere [7]. It must be stressed that care was taken to operate with highly dehydrated substances and their mixtures.

2. Ebulliometric method of measurements

The ebulliometric method consists in observing the changes both in the boiling and in the condensation temperatures each time a known

quantity of one of the components is added. Two Świątosławski ebulliometers were used for this purpose. A simple one filled with water served for measuring the pressure changes and a differential one, composed of three sections, was used for determining the boiling temperature and also the two condensation temperatures of the liquid vapour system under examination. The results obtained are listed in Table I. In column I are listed the boiling temperatures of the various azeotropes examined, in column II — the composition of each azeotropic mixture, expressed in weight percentage of *A* (%*G*), and in column III the azeotropic depressions calculated with respect to the lower boiling component.

TABLE I

Substances		I	II	III
Acetic acid <i>A</i>	— (118.05)	—	—	—
„ „	<i>n</i> -hexane (68.60)	68.25	6.0	0.35
„ „	<i>n</i> -heptane (98.25)	91.72	33.0	6.53
„ „	<i>n</i> -octane (125.30)	105.70	53.0	12.35
„ „	<i>n</i> -nonane (150.20)	112.80	69.0	5.25
„ „	<i>n</i> -decane (173.30)	116.75	79.5	1.30
„ „	<i>n</i> -undecane (193.85)	117.72	95.0	0.33

It can be seen that the shapes of the corresponding isobars are very flat, especially in the vicinity of the azeotropic points. With an increase in the boiling temperature of the homologue, the flat shape of the isobars becomes more distinctly pronounced and approaches that of the isobars characteristic for typical binary heteroazeotropes. This may be illustrated by the following example: the mixtures of acetic acid and *n*-nonane, containing from 22.5 to 41 weight per cent of nonane, boil within the narrow range of temperature of 0.15° C.

In addition, it should be noted that the sections of the isobars lying near the corresponding azeotropic points are asymmetrical.

The flat shape of all the isobars examined is probably due, to some extent at least, to the restricted mutual solubility of the components. At room temperature the mixtures formed by normal paraffins (ranging from *n*-hexane to *n*-octane) with acetic acid are homogeneous, whereas the higher boiling paraffins form with acetic acid two liquid phase systems.

The azeotropic range of acetic acid is very large:

$$Z_A(H) = t_{H_k} - t_{H_e} = 193.85 - 68.6 = 125.25^\circ \text{C}.$$

In this equation t_{H_k} and t_{H_e} are the respective boiling temperatures of *n*-undecane, *U*, and *n*-hexane, *H_e*; it should be stressed that both these hydrocarbons form almost tangent "azeotropic" isobars.

The boiling temperatures of the two azeotropes are

$$t_{(Ac,U)} = t_{Ac} - 0.33^\circ \text{C.}$$

and

$$t_{(Ac,H_e)} = t_{H_e} - 0.35^\circ \text{C.},$$

t_{Ac} , $t_{(Ac,U)}$ and $t_{(Ac,H_e)}$ being the normal boiling temperatures of acetic acid and of the two azeotropes formed by acetic acid with *n*-undecane

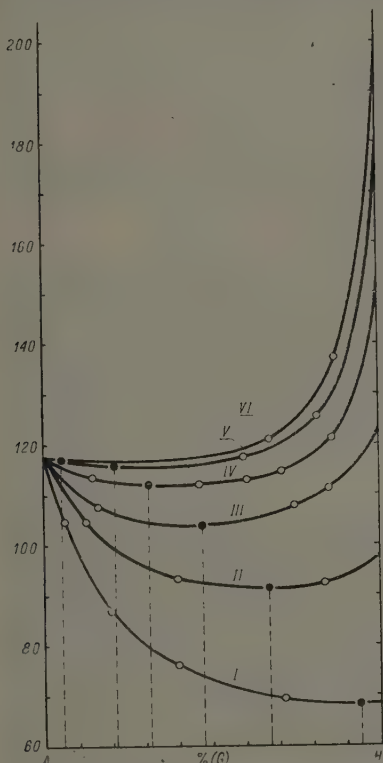


Fig. 1. Boiling temperature isobars formed by acetic acid *A* with paraffin hydrocarbons (*H*). Curves from I to VI represent the isobars formed by acetic acid with paraffins ranging from *n*-hexane (I) to *n*-undecane (VI). Because of lack of space, several points only are given on curves V and VI, instead of the large number of points established experimentally

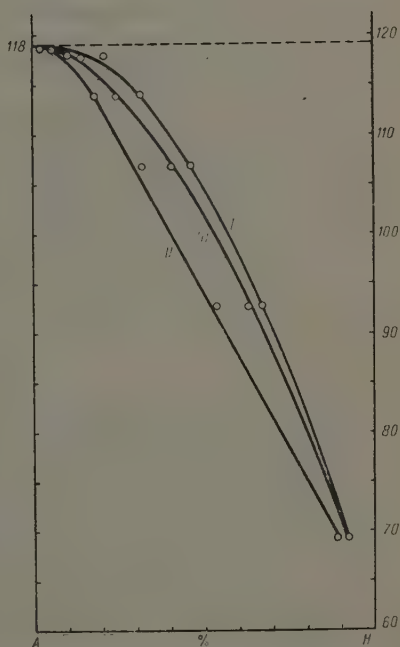


Fig. 2. Curves I to III represent the relation between the boiling temperatures of azeotropic mixtures as a function of the composition of *A*: in weight (I), mole (II) and volume (III) percentages

or *n*-hexane. The neighbouring representatives: the lower boiling *n*-pentane and the higher boiling *n*-dodecane form with acetic acid typical "zeotropic mixtures".

To get tangent isobars for mixtures of Ac and U and of Ac and H_e , the pressure under which the isobar has to be examined should be changed correspondingly.

It may be seen below that the azeotropic range $Z_A(H)$ is characterized by a large degree of asymmetry. In fact, in its lower portion $t_{Ac} - t_{H_e}$ is equal to $49.5^\circ C.$ and in its upper one $t_U - t_{Ac} = 75.8^\circ C.$

As to the shapes of the isobars shown in Fig. 1 they are asymmetrical with respect to their azeotropic points. This indicates that the fractional distillation method of preparing azeotropes may give rise to errors. In fact, the flat and asymmetrical character of the isobars does not favour a sharp separation of the fraction representing the exact composition of the azeotrope obtained by distillation. For this reason, in determining the exact composition and the boiling temperatures of azeotropes formed by acetic acid with hydrocarbons, the ebulliometric method offers better results than the distillation method.

In Figure 2 the shape of curve II representing the relation between changes in the azeotropic temperatures of the respective mixtures as a function of composition (mols per cent) cannot be presented by using an empirical equation similar to those suggested by H. Skolnik [8] for other azeotropes. In this case better results might have been obtained if an equation similar to that used by Lecat [9] had been applied.

I wish to express my thanks to Professor W. Świątosławski for his help and advice.

Summary

1. The boiling temperature isobars formed by mixtures of acetic acid with normal paraffins, ranging from n -hexane to n -undecane, were ebulliometrically examined. The boiling temperature and the composition of each azeotrope are listed in Table 1.
2. Experiments have shown that the isobars are characterized by very flat sections in the vicinity of the azeotropic points.
3. Normal hexane is the lowest and normal undecane the highest boiling paraffin forming almost tangent "azeotropic" isobars with acetic acid.
4. All the isobars are characterized by asymmetry of the sections lying near the point representing the composition of the azeotropic points.
5. The lower portion of the azeotropic range is much smaller ($45^\circ C.$) than the upper one ($75^\circ C.$).

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Ideal eutectic systems

by

W. MALESIŃSKI

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of December 13, 1954

1. General assumptions

Let us consider a series of two- three- or multicomponent systems formed by any organic compounds which do not react with each other and do not form intermolecular complexes. Let them form so-called simple eutectic systems in which the liquid homogeneous phase is in equilibrium with the solid phases, each solid phase consisting of a pure component.

In order to determine the equilibrium temperatures in the whole concentration range it is necessary to know the relations determining the partial freezing temperatures of each component, depending in general on all the mole fractions of the components. In general the relations mentioned above are different for each of the components, depending upon the chemical character of the other components composing the system. Because we are unable to describe these relations in general terms, we are forced to determine experimentally the parameters defining the equilibrium state of the system.

The problem becomes more simple when a series of eutectic systems is formed by chemically related compounds characterized by similar physicochemical properties. In connexion with this we suggest the division of all organic compounds forming simple eutectics into groups formed

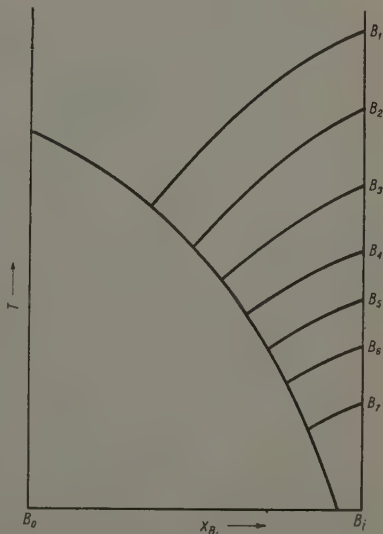


Fig. 1. Świątosławski's scheme for a series of eutectics formed by component B_0 and a series of compounds closely related chemically.

by similar, chemically related compounds. Below we will consider exclusively systems composed of such compounds.

According to Świątosławski's [1] assumption, the partial freezing temperature of a given component depends exclusively upon its mole fraction in the solution and is not influenced by any other relations associated with the coexistence of other components of the system. In Fig. 1 these simplified relations are shown on a diagram.

Hence we may assume the existence of a certain function expressing the relation between the partial freezing temperature of the given component and its concentration. This function will, of course, determine the ideal curve of solubility.

2. Eutectic systems formed by chemically related compounds

Penkala has recently collected [2] experimental data showing that, in the first approximation, Świątosławski's assumption seems to be correct. On the basis of these facts further conclusions may be drawn for systems in which the components belong to the same group of structurally and

chemically related substances. First of all, two compounds belonging to the same series and both having the same freezing temperature are characterized by the same ideal solubility curve (Fig. 2 substance B_1 and B_2). Next, when two components B_1 and B_2 , for example, forming a two-component eutectic mixture $E_{B_1B_2}$ have the same freezing temperature: $T_{B_1} = T_{B_2}$, the solubility curves of the eutectic mixture $E_{B_1B_2}$ and of the pure component B_3 are identical, if the freezing temperatures of B_3

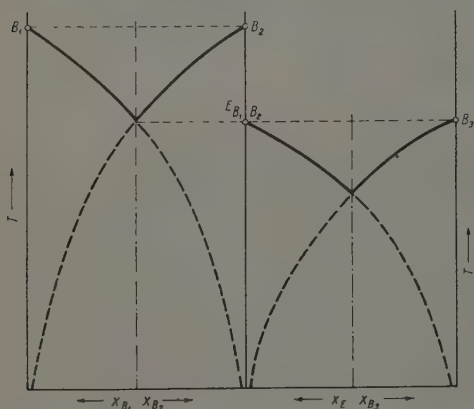


Fig. 2. Branches of a eutectic system formed by a pure component B_3 and a binary eutectic mixture $E_{B_1B_2}$, where $T_{B_3} = T_{E_{B_1B_2}}$ and $T_{B_1} = T_{B_2}$.

and $E_{B_1B_2}$ are equal ($T_{B_3} = T_{E_{B_1B_2}}$). This relation is graphically represented in Fig. 2.

The conclusions given above may be treated as a basis for constructing a model of a hypothetical multicomponent eutectic system, in which all the components will have equal freezing temperatures. Assuming, just as for the two-component eutectic mixture $E_{B_1B_2}$, the identity of ideal solubility curves of pure components and those of multicomponent eutectic mixtures, if only the freezing temperatures of the pure component

and of the eutectic mixture are equal, one can show the correspondence between the constructed model of a hypothetical system and that of a real system whose components are characterized by different freezing temperatures.

3. Further consequences

The considerations mentioned above, as well as the analysis of the model, lead to the conclusion that for a given series of chemically related compounds a universal function may be found embracing all the solubility curves:

$$(1) \quad T'_1 = f\left(\frac{x_i}{m_i}\right).$$

In this equation T'_1 stands for the partial freezing point of component i , x_i — denotes the concentration of that component, m_i — is a constant for the given component i and will be called a eutectic parameter of component i . Thus m_i does not depend upon the temperature. The validity of equation (1) depends on the degree of approximation introduced by the above assumptions. The use of this function should make it possible to determine the relation between the partial freezing temperatures and the composition of all the compounds involved. Function f should be considered as an unknown universal function characterizing the whole series of compounds under consideration. It is a function of one variable and may be represented by the ideal solubility curve. The stable part of the solubility curve in a given system fixed by the freezing temperatures of the pure component and of the eutectic mixture, may also be called a eutectic branch of component i . In the case of a three-component system the universal function (1) may be graphically represented by a cylindrical surface on a tridimensional diagram T, x_2, x_3 , for k -component eutectic systems it will be represented by a hypersurface on a k -dimensional diagram.

Parameter m_i is defined by the limit conditions of relation (1). For $T'_1 = T_i$, where T_i corresponds to the freezing temperature of the pure component i , $x_i = 1$. Consequently

$$(2) \quad T_i = f\left(\frac{1}{m_i}\right); \quad m_i = \frac{1}{f^{-1}(T_i)};$$

where f^{-1} is reversed with respect to f , so that if $y = f(n)$, then $n = f^{-1}(y)$.

4. Conclusions

On condition that the freezing temperatures of the pure components are known, and that either the universal function or one of the solubility curves or even one branch of the eutectic system for a given component is known, it is possible to determine in a given range of temperature, the ideal solubility curves for all the components. In this way, too, it is

possible to give a full description of the equilibrium parameters for all of the two-three-and multicomponent eutectic systems formed by a series of chemically and structurally related substances.

We apply the term *ideal eutectic systems* to those simple eutectic systems which are composed of the above series of compounds, for which the equilibrium parameters are determined by the universal relation (1) expressing all the solubility curves. So equation (1) and the universal character of function f are the criteria of the ideality of a multicomponent eutectic system.

Summary

1. It is suggested to divide all organic compounds forming simple eutectic systems into groups of chemically related compounds.

2. A type of simple multicomponent eutectic system, formed by compounds closely related chemically, and called an ideal eutectic system, was described.

3. It was shown that in an ideal eutectic system a universal relation (1), determining the ideal solubility curves of individual components, is fulfilled.

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Une nouvelle méthode de détermination des coordonnées hypocentrales d'un séisme rapproché

par

E. W. JANCZEWSKI

Présenté par J. SAMSONOWICZ à la séance du 22 Novembre 1954

Pour éviter certaines ambiguïtés dans le calcul des coordonnées de l'hypocentre d'un séisme rapproché et pour éliminer les divergences assez sensibles qui affectent les résultats obtenus par les méthodes de G. Schmerwitz [1] et de P. Caloi [2], nous appliquons une méthode différente, bien que fondée sur les mêmes principes et les mêmes simplifications. Toutefois, dans les limites de l'exactitude requise en pratique, nous jugeons admissible de traiter en observations indépendantes deux des données pouvant être déduites des enregistrements d'une station, l'une mesurant la durée de l'intervalle entre les phases Pg et Sg , l'autre — le temps (absolu) du début de Sg .

Soient x_0, y_0, z_0 les coordonnées rectangulaires (de Soldner) de l'hypocentre, t_0 le temps (absolu) du choc initial en ce point; soient x_i, y_i, z_i les coordonnées d'une station S_i quelconque (son altitude est habituellement négligeable, $z_i \approx 0$) où, au moment t_i , arrive l'onde Sg qui se propage avec la vitesse V , constante mais inconnue. On aura:

$$(1) \quad F_i = \frac{\Delta_{hi}}{V} - (t_i - t_0) = 0; \quad \Delta_{hi} = \sqrt{(x_i - x_0)^2 + (y_i - y_0)^2 + z_i^2}$$

$$(i=1, 2, \dots, m)$$

D'autre part chaque observation de l'intervalle T_j entre les phases Pg et Sg à la station S_j , dont les coordonnées sont x_j, y_j , nous donnera une équation:

$$(2) \quad F_j = \frac{\Delta_{hj}}{k} - T_j = 0, \quad \Delta_{hj} = \sqrt{(x_j - x_0)^2 + (y_j - y_0)^2 + z_0^2},$$

où $k = (V_P \cdot V_S) : (V_P - V_S)$, V_P = vitesse de l'onde Pg , V_S = vitesse de l'onde Sg .

Choisissons un système de valeurs approchées: $(x_0), (y_0), (z_0), (V), (t_0), (k)$ et posons:

$$(3) \quad \begin{aligned} x_0 &= (x_0) + x, & y_0 &= (y_0) + y, & z_0 &= (z_0) + z, \\ V &= (V) + v, & t_0 &= (t_0) + \tau, & k &= (k) + \kappa \end{aligned}$$

où x, y, z, v, τ, κ sont de petites corrections qu'il faudra déterminer par le calcul de compensation après avoir réduit les équations (1) et (2) à la forme linéaire.

Le développement de F_i en série de Taylor, limité aux termes du premier ordre, donne:

$$(4) \quad F_i = F_i(0) + \frac{\partial F_i(0)}{\partial(x_0)} \cdot x + \frac{\partial F_i(0)}{\partial(y_0)} \cdot y + \frac{\partial F_i(0)}{\partial(z_0)} \cdot z + \frac{\partial F_i(0)}{\partial(V)} \cdot v + \frac{\partial F_i(0)}{\partial(t_0)} \cdot \tau,$$

où:

$$\begin{aligned} \frac{\partial F_i(0)}{\partial(x_0)} &= \frac{(x_0) - x_i}{(V)(\Delta_{hi})} = a_i; & \frac{\partial F_i(0)}{\partial(y_0)} &= \frac{(y_0) - y_i}{(V)(\Delta_{hi})} = b_i; \\ \frac{\partial F_i(0)}{\partial(z_0)} &= \frac{(z_0)}{(V)(\Delta_{hi})} = c_i; & \frac{\partial F_i(0)}{\partial(V)} &= -\frac{(\Delta_{hi})}{(V)^2} = d_i; \\ \frac{\partial F_i(0)}{\partial(t_0)} &= 1 = e_i; & F_i(0) &= \frac{(\Delta_{hi})}{(V)} - (t_i - (t_0)) = l_i; \\ (\Delta_{hi}) &= \sqrt{(x_i - (x_0))^2 + (y_i - (y_0))^2 + (z_0)^2} \end{aligned}$$

On trouvera de façon tout à fait analogue:

$$\begin{aligned} (5) \quad F_j &= F_j(0) + \frac{\partial F_j(0)}{\partial(x_0)} \cdot x + \frac{\partial F_j(0)}{\partial(y_0)} \cdot y + \frac{\partial F_j(0)}{\partial(z_0)} \cdot z + \frac{\partial F_j(0)}{\partial(k)} \cdot \kappa \\ \frac{\partial F_j(0)}{\partial(x_0)} &= \frac{(x_0) - x_j}{(k)(\Delta_{hj})} = a_j; & \frac{\partial F_j(0)}{\partial(y_0)} &= \frac{(y_0) - y_j}{(k)\Delta_{hj}} = b_j; \\ \frac{\partial F_j(0)}{\partial(z_0)} &= \frac{(z_0)}{(k)(\Delta_{hj})} = c_j; & \frac{\partial F_j(0)}{\partial(k)} &= -\frac{(\Delta_{hj})}{(k)^2} = f_j; \\ F_j(0) &= \frac{(\Delta_{hj})}{(k)} - T_j = l_j; & (\Delta_{hj}) &= \sqrt{(x_j - (x_0))^2 + (y_j - (y_0))^2 + (z_0)^2}. \end{aligned}$$

Il en résulte un système de $m+n$ équations linéaires:

$$(6) \quad a_i x + b_i y + c_i z + d_i v + e_i \tau + l_i = v_i \quad (i=1, 2, \dots, m),$$

$$(7) \quad a_j x + b_j y + c_j z + f_j \kappa + l_j = v_j \quad (j=m+1, m+2, \dots, m+n),$$

dont la solution peut être trouvée soit directement, par la méthode des cracoviens, soit indirectement au moyen de l'algorithme de Gauss, après avoir calculé les coefficients des équations normales:

$$\begin{aligned} (8) \quad [aa]x + [ab]y + [ac]z + [ad]v + [ae]\tau + [af]\kappa + [al] &= 0 \\ [bb]y + [bc]z + [bd]v + [be]\tau + [bf]\kappa + [bl] &= 0 \\ [cc]z + [cd]v + [ce]\tau + [cf]\kappa + [cl] &= 0 \\ [dd]v + [de]\tau + [df]\kappa + [dl] &= 0 \\ [ee]\tau + [ef]\kappa + [el] &= 0 \\ [ff]\kappa + [fl] &= 0. \end{aligned}$$

Les erreurs moyennes des corrections $x, y, z, v, \tau, \varepsilon$ seront calculées au moyen des formules habituelles:

$$(9) \quad \begin{aligned} m_x &= \sqrt{\frac{[vv]}{(m+n-6)[aa \cdot 5]}}; & m_y &= \sqrt{\frac{[vv]}{(m+n-6)[bb \cdot 5]}}; \\ m_z &= \sqrt{\frac{vv}{(m+n-6)[cc \cdot 5]}}; & m_v &= \sqrt{\frac{[vv]}{(m-5)[dd \cdot 5]}}; \\ m_\tau &= \sqrt{\frac{[vv]}{(m-5)[ee \cdot 5]}}; & m_\varepsilon &= \sqrt{\frac{[vv]}{(n-4)[ff \cdot 5]}}. \end{aligned}$$

Exemple d'application de la méthode. Tremblement de terre du 31 janvier 1935 dans les environs de Constance. Origine des coordonnées: $\varphi = 47^\circ 42.0' N$, $\lambda = 9^\circ 01.0' E$. Phases Pg et Sg citées d'après W. Hiller [3].

	x	y	Pg	Sg
1. Ravensburg	+ 44.7 km	+ 9.7 km	13h39m39.0s	13h39m44.4s
2. Zurich	— 32.95	— 36.75	39.6	46.0
3. Messtetten	— 4.04	+ 53.55	40.1	47.6
4. Bâle	—108.0	— 16.8	50.5	40 04.1
5. Stuttgart	+ 13.0	+119.1	51.95	07.0
6. Karlsruhe	— 44.1	+145.95	58.0	17.0
7. Neuchâtel	—156.3	— 76.0	40 01.9	23.8

Après avoir choisi pour valeurs approchées:

$$(x_0) = +1.0, \quad (y_0) = 0.0, \quad (z_0) = 10.0, \quad (V) = 3.32,$$

$$(t_0) = 13^h 39^m 30.9^s, \quad (k) = 8.20,$$

nous calculons d'abord les coefficients des équations linéaires (6) et (7), ensuite ceux des équations normales:

$$\begin{aligned} 0.3416x + 0.0998y + 0.01441z - 8.053v + 0.5671\tau - 0.5409\varepsilon - 0.1687 &= 0 \\ 0.3828y - 0.03011z + 5.431v - 0.5508\tau + 0.3605\varepsilon + 0.1909 &= 0 \\ 0.03373z - 2.869v + 0.4034\tau - 0.1904\varepsilon - 0.0029 &= 0 \\ 728.0 \quad v - 64.46 \quad \tau \quad 0 &\quad -0.9615 = 0 \\ &\quad 6.000 \quad \tau \quad 0 \quad +0.4152 = 0 \\ &\quad 19.56 \quad \varepsilon + 3.7624 = 0 \\ &\quad 1.6394 = [U] \end{aligned}$$

La solution donne des valeurs suffisamment petites pour les corrections cherchées:

$$\begin{aligned} x &= +0.782, & y &= -0.778, & z &= -2.18, \\ v &= +0.0241, & \tau &= +0.192, & \varepsilon &= -0.178, \end{aligned}$$

qui, en vertu des relations (3), déterminent les valeurs définitives de toutes les six inconnues de notre problème.

Le tableau ci-dessous contient les résultats de nos calculs mis en regard des résultats correspondants publiés auparavant par Schmerwitz [1] et Caloi [4]

	Janczewski 1954	Caloi 1942	Schmerwitz 1938	
			sur Pg	sur Sg
x_0	$+ 1.78 \pm 0.84$	$+ 4.35 \pm 0.84$	$+ 0.8 \pm 0.8$	$+ 1.3 \pm 1.3$
y_0	$- 0.78 \pm 0.67$	$- 2.99 \pm 2.07$	$+ 0.6 \pm 0.8$	0.0 ± 1.3
z_0	7.81 ± 1.13	15.8 ± 5.65	posé = 0	11 ± 13
h	8.022 ± 0.127	8.204 ± 0.153		3.32 ± 0.03
V_S	3.344 ± 0.021			
V_P			5.65 ± 0.02	
t_0	$13^h 39^m +$ $31.09^s \pm 0.68$		30.90 ± 0.2	30.75 ± 1.1

Il faut noter que Caloi, pour déterminer les quatre inconnues dans ses calculs, basés sur les formules (2), (5) et (7), s'était servi des intervalles T_j notés par sept stations, tandis que dans notre problème, pour trouver six inconnues, nous disposons de quatorze données provenant des mêmes stations que chez Caloi.

Les neuf observations de Pg dont disposait Schmerwitz ne lui ayant pas permis de résoudre le problème, cet auteur se contenta d'une solution partielle en posant arbitrairement $z_0 = 0$. La variante basée sur onze observations de Sg lui a permis d'obtenir une solution complète, bien que peu précise.

En comparant les valeurs de z_0 déterminées par chacune des trois méthodes en usage jusqu'à présent, on constate des divergences déconcertantes qui semblent interdire tout essai de fixer la profondeur de ce séisme mieux qu'à 10 km près.

Pour juger de la probabilité de notre résultat, $z_0 = 7.81 \pm 1.13$ km, il faut remarquer que la moyenne déduite des trois positions du foyer, calculées suivant les méthodes anciennes, correspond à un point situé à environ un kilomètre de l'hypocentre. L'ordre de grandeur de cette distance étant pareil à celui des erreurs moyennes des coordonnées, trouvées d'après la nouvelle méthode, fait apercevoir les avantages pratiques de celle-ci et permet d'estimer le degré d'exactitude des résultats que nous avons obtenus dans le cas présent.

Toutefois, à propos des erreurs moyennes calculées au moyen des formules classiques de la théorie des moindres carrés, il ne faut pas oublier qu'elles ont une signification précise seulement dans le cas où les observations sont indépendantes, très nombreuses et libres d'erreurs systéma-

tiques. De telles conditions n'étant jamais entièrement réalisables dans la pratique, la grandeur de ces erreurs ne peut avoir qu'une signification relative.

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